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JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY

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JOSEPH J. KATZ: *Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, U.S.A.*
A. G. MADDOCK: *University Chemical Laboratory, Lensfield Road, Cambridge, England*
L. E. J. ROBERTS: *Atomic Energy Research Establishment, Harwell, Didcot, Berks, England*
E. J. W. VERWEY: *Philips Research Laboratories, Eindhoven, The Netherlands*

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NEW LIGHT ISOTOPES OF THALLIUM PRODUCED BY BOMBARDMENT OF TUNGSTEN WITH NITROGEN IONS

K. F. CHACKETT and G. A. CHACKETT
Physics Department, University of Birmingham

(*Received* 28 *May* 1959)

Abstract—Two new thallium isotopes of half-lives 10 min and 30 min have been found among products of the bombardment of tungsten with nitrogen ions in the Nuffield cyclotron of the University of Birmingham. Identification and mass assignments depend on the decay curves of radio-chemically separated samples. The 10 min activity is assigned to ^{191}Tl and the 30 min activity to ^{193}Tl. Decay proceeds almost entirely by electron capture; α-particle emission has not been detected.

IN continuation of our work on the heavy-ion bombardment of elements in the region of tantalum[1] we now report results obtained using similar techniques with tungsten as the target. The energy spectrum of the nitrogen ion beam has a peak at about 60 MeV, which is close to the Coulomb-barrier height, and the relative number of ions of greater energy falls off quite rapidly. In these circumstances the most probable nuclear reaction is the evaporation of five neutrons from the compound nucleus. Evaporation of a smaller, or a larger, number of neutrons will occur with markedly less probability. The experimental results with tantalum are consistent with these predictions.

Since normal tungsten consists of the stable isotopes ^{180}W (0·14%), ^{182}W (26·4%), ^{183}W (14·4%), ^{184}W (30·6%), and ^{186}W (28·4%), one would expect the lightest thallium isotope produced in good yield to be ^{191}Tl from the reaction ^{182}W(N,5*n*)^{191}Tl. At the other end of the scale one would expect ^{195}Tl from ^{186}W(N,5*n*)^{195}Tl; until now this has been the lightest known thallium isotope.

EXPERIMENTAL

Bombardments. Thin metallic tungsten foils were bombarded for periods ranging from a few minutes to 2 hr in the way already described elsewhere.[1,2] Immediately after bombardment radio-chemical separations of thallium, mercury and gold were made and thinly-spread samples were counted under standard end-window G.M. tubes. In addition bombardments were made of tungstic oxide cemented to the inner current probe with a small quantity of nylon, using a 10 μ thick aluminium-window on the outer probe. In some of these experiments the tungstic oxide had been enriched to 98 per cent in the isotopes ^{182}W or ^{184}W.* Beam currents were sufficient to give initial counting rates of a few thousand counts per minute from samples separated from foil targets. Smaller beam intensities were necessary with the oxide targets and this resulted in initial counting rates of only about 100 c.p.m., except for the mercury fraction from ^{182}W which had an initial counting rate of 600 c.p.m.

Chemical separations. After bombardment the targets were quickly dissolved in hot nitric acid-hydrofluoric acid mixture containing 100 γ of carriers for Tl, Hg, Au and Pt. When solution was complete more carriers were added making up the amounts to 2 mg. After a few minutes heating to ensure chemical equilibrium, solvent extraction with amyl acetate was carried out, removing practically all the thallium, mercury and gold. The extract was separated and washed with ammonium

* Enriched tungsten isotopes were supplied by A.E.R.E., Harwell.

[1] K. F. CHACKETT and G. A. CHACKETT, *J. Inorg. Nucl. Chem.* **4**, 225 (1957).
[2] K. F. CHACKETT, J. H. FREMLIN and D. WALKER, *Phil. Mag.* **45**, 173 (1954).

chloride–hydrochloric acid mixture. The aqueous extract was diluted and mercuric sulphide precipitated from it. The remaining amyl acetate was evaporated to dryness and the residue taken up with hydrochloric acid. From this solution gold was precipitated with hydrazine and sulphur dioxide, and thallous iodide with potassium iodide.

When time permitted each separated sample was purified by addition of inactive hold-back carriers and further chemical processing, but the cross-contamination in the simple separation process appears to have been quite small.

The precipitates were mounted on filter paper disks for counting; alternatively thallium fractions were sometimes re-dissolved in *aqua regia* and extracted into amyl acetate. From this solution samples of mercury were milked at fixed intervals by washing with slightly acid ammonium chloride solution containing about 1 mg of mercury carrier. Mercuric sulphide was obtained from each extract and mounted for counting in the usual way.

Counting. End-window halogen-quenched G.M. tubes were used to count the samples. Decay of isotopes in this region of N and Z is largely by electron capture to excited states of the product nuclei followed by highly converted γ-ray emission.[3] Thin windowed G.M. tube counters are therefore far from ideal since the complexity of the decay schemes and the softness of the conversion electrons makes it difficult to estimate counting efficiencies, but they are adequate for the study of half-lives and genetic relationships. The short-lived thallium isotopes described in this paper, as well as some of the mercury and gold daughter products, could however be detected using aluminium absorbers sufficient to absorb electrons of 500 keV energy, so that it is possible that these isotopes also decay by positron emission. Annihilation radiation from bombarded tungsten was looked for using a sodium iodide crystal and single channel analyser but could not be positively identified in the complex spectrum of nuclear γ-rays.

Annihilation radiation was detected from samples of separated thallous iodide by using two sodium iodide scintillators in coincidence. In this arrangement maximum geometrical efficiency was obtained by sandwiching the sample between two beryllium plates 1 mm thick and placing this in close contact with two sodium iodide crystals 1½ in. in diameter and 1 in. thick. In view of the complex nature of the nuclear γ-ray spectra, a rather narrow channel width (10 per cent of the pulse height) was used, and coincident pulses within this range in both detectors were recorded. With this arrangement the absolute efficiency for detection of annihilation radiation is quite low (of the order 0·1 per cent), but the natural background is only a few counts per hour.

None of the separated samples emitted α-particles detected by a zinc sulphide scintillation counter to the extent of one α-particle per 1000 detected conversion electrons.

RESULTS AND DISCUSSION

The results may be most conveniently summarized by stating the periods found by resolution of the decay curves of the gold, mercury and thallium samples in turn (see Table 1).

TABLE 1.—LIGHT Tl, Hg, Au AND Pt ISOTOPES. TAKEN FROM THE G.E.C. CHART OF THE NUCLIDES (1956 EDITION) WITH THE ADDITION OF ^{191}Tl, ^{192}Tl, MODIFICATION OF HALF-LIFE OF ^{198}Au[1] AND ^{196}Tl[4]

		^{191}Tl 10 min		^{193}Tl 30 min		^{195}Tl 1·2 hr	^{196}Tl 2·4 hr
	^{189}Hg 23 min	^{190}Hg 90 min ?	^{191}Hg 57 min	^{192}Hg 5·7 hr	^{193}Hg 12 hr/4 hr	^{194}Hg 0·4 sec/180 day	^{195}Hg 9·5 hr
^{187}Au 15 min	^{188}Au 4·3 min	^{189}Au 42 min	?	^{191}Au 3·0 hr	^{192}Au 4·8 hr	^{193}Au 17 hr	^{194}Au 39 hr
	^{187}Pt 2·5 hr	^{188}Pt 10·5 days	^{189}Pt 10·5 hr	^{190}Pt Stable	^{191}Pt 3·0 days	^{192}Pt Stable	^{193}Pt 4·5 days

[3] L. P. GILLON, K. GOPOLA KRISHNAN, A. DE-SHALIT and J. W. MIHELICH, *Phys. Rev.* **93**, 124 (1954).
[4] G. ANDERSSON, E. ARRMAN and B. JUNG, *Arkiv. Fysik* **11**, 297 (1957).

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Gold samples. Found: 3–6 days (weak); 17 hr; 3–4·5 hr. The long weak component, about 1 count/min above background, we ascribe to platinum daughters ^{191}Pt and ^{193}Pt. The 17 hr component is ascribed to ^{193}Au and the shorter component to mixtures of ^{191}Au (3·0 hr) and ^{192}Au (4·8 hr) depending on the length of bombardment time and the interval before separation from parent mercury. No shorter periods were found.

Mercury samples. Found: about 3 days; 15 hr; 4·5 hr; 1 hr. As in the gold, the long component is thought to be a mixture of platinum daughters. We believe that the 15 hr component represents the daughter 17 hr ^{193}Au decay mixed with shorter components impossible to resolve from it. Such might be (a) the 12 hr ^{193m}Hg, detected perhaps also by decay of its 4 hr ^{193}Hg daughter (b) the complex decay of ^{192}Hg (5·7 hr) decaying to ^{192}Au (4·8 hr) which, (assuming equal detection efficiency of these isotopes) would decay to half its initial rate in 15 hr, the half-life eventually decreasing to 5·7 hr; (c) the 9·5 hr ^{195}Hg. Clearly great care would be necessary to permit firm conclusions to be drawn from such an extremely complicated mixture. However the 4·5 hr component seems to confirm the existence of the 193 chain (^{193}Hg 4 hr). Also we can only ascribe the 1 hr component to ^{191}Hg (57 min).

The mercury fractions obtained in the milking experiments were very similar to the above except that the proportion of 1 hr component decreased in later samples. From experiments with milking intervals of 10 min, 15 min and 30 min, we concluded that the 1 hr component must have a Tl parent of half-life 10 min. The experiment with a 30 min milking interval showed that the intensities of the 4·5 hr and 15 hr components were reduced by a factor of about two in the successive mercury fractions. We therefore infer the existence of ^{193}Tl with a period of 30 min. We can make no deductions from these experiments about the possible existence of ^{192}Tl.

Mercury fractions obtained from bombarded ^{184}W gave somewhat more of the 1 hr component relative to the others, and those from ^{182}W more still. Also instead of a 15 hr component this now appeared to be 13 hr, presumably due to an increasing proportion of the 192 chain (not of the 195 chain, which should not be present). Indeed we could not expect in the ^{182}W bombardments the formation of mercury isotopes as heavy as ^{193}Hg since evaporation of only three neutrons is highly unlikely on energetic grounds. If such a reaction could occur we would expect to find ^{196}Tl and ^{197}Tl from the natural mixture of tungsten isotopes, and these we did not detect.

Thallium samples. Thallium samples obtained after bombardment of the natural tungsten isotopes showed a very complex decay on an end-window G.M. counter, with components of about 1 hr and about 10 hr predominating. Smaller amounts of activities of intermediate half-life were present and a shorter component apparently of rather less than half an hour period, but itself clearly a mixture.

In an effort to reduce the difficulty of interpretation, counting was also carried out with the sources under various thicknesses of aluminium absorber. Both with 88 mg/cm^2 and 210 mg/cm^2 absorbers the decay curves could now be resolved with much more certainty and periods 10 hr, 4·5 hr, 30 min and 10 min were found. While the former pair of activities may be ascribed to daughters and are themselves complex, the 30 min and 10 min periods could only be assigned to new activities in thallium. The latter values depend somewhat on the assumptions made about the periods of the daughter activities, but the extent of the dependence is small because of the much greater initial counting rates (by a factor 20 : 1) between the 30 min and the 4·5 hr

components. Resolution of the two decay curves by taking a variety of values for the half-lives of the daughter components, consistent with the data, all gave values for the shorter components of 10 ± 1 and 30 ± 3 min. The half-lives calculated from the other experiments agree with these within experimental error given by the counting statistics.

From the decay curves of thallium samples so far described it was not possible to decide whether the 1 hr component found in the curves obtained without absorbers was due to the 1·2 hr ^{195}Tl formed, e.g. in the reaction ^{186}W(N,5*n*)^{195}Tl, or whether a short-lived ^{191}Tl isotope was decaying into 57 min ^{191}Hg as inferred from the milking experiment. Probably both chains were present. A bombardment of ^{182}W was carried out to confirm the presence of ^{191}Tl and the thallium fraction did indeed show a strong 10 min period followed by a 1 hr component, together with a weak component of about 12 hr half-life. The latter is probably due to members of the 192 chain, implying the existence of ^{192}Tl, but the counting rates were far too low for a firm statement to be made.

The bombardment of ^{184}W gave a thallium fraction which decayed with 30 min, 4·0 hr and 17 hr periods, confirming that 30 min ^{193}Tl is the parent of 4 hr ^{193}Hg. It is significant that the resolution of this decay curve was much easier than was the case for the mercury fraction from the same bombardment. This is because the thallium fraction would contain only the 193 mass chain if we may assume a short half-life for ^{192}Tl, whereas the mercury fraction would contain both the 192 and 193 mass chains.

Experiments with the coincidence scintillation counter showed that the thallium formed by bombardment of the natural mixture of tungsten isotopes emitted positrons with periods of 10 min and 30 min, followed by other activities of much longer period. Thus while this observation confirms the existence of the two new thallium isotopes both of which evidently decay partly by positron emission, the low counting rates obtained do not permit any conclusion about the genetic relationship with the daughter isotopes.

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CONCLUSIONS

The results show the existence of at least two new thallium isotopes; ^{191}Tl (10 ± 1 min) and ^{193}Tl (30 ± 3 min). Decay is largely by electron capture but positron emission also occurs. The formation process is by reactions such as ^{182}W(N^{14},5*n*)^{191}Tl and ^{184}W(N^{14},5*n*)^{193}Tl. It is possible that ^{192}Tl and ^{194}Tl are also formed but we have no direct evidence about these isotopes.

We should like to mention that members of the 194 mass chain have also been sought but without success by bombardment of rhenium with carbon and nitrogen ions The latter have been shown to yield the recently discovered ^{195}Pb (17 min) and ^{196}Pb (37 min).[4] It seems probable that the use of heavy ion beams of high intensity might lead to several more new isotopes in this region.

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CROSS-SECTIONS FOR THE REACTIONS $^{226}Ra(n,2n)^{225}Ra$ AND $^{226}Ra(n,3n)^{224}Ra$ WITH 14·5 MeV NEUTRONS

L. P. O'Connor and J. L. Perkin
Atomic Weapons Research Establishment, Aldermaston, Berks

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Abstract—About 5 mg of ^{226}Ra were irradiated with 14·5 MeV neutrons. The products of the $^{226}Ra(n,2n)^{225}Ra$ and $^{226}Ra(n,3n)^{224}Ra$ reactions were determined by isolating ^{209}Pb and ^{213}Bi from their respective decay chains.

^{209}Pb was isolated by separating ^{213}Bi from the radium by means of an electrochemical deposition and then allowing ^{209}Pb to grow in from its decay chain. ^{209}Pb was then separated and its β-particle activity was counted in a 4π proportional counter. ^{213}Bi was obtained by an electrochemical deposition following an electrolytic deposition of ^{213}Pb. The α-particle activity of ^{213}Bi was counted in a gridded ionization chamber.

The values found for the cross-sections are as follows—

$$^{226}Ra\ \sigma\ (n,2n) = 1{\cdot}60 \pm 0{\cdot}20\ \text{barn}$$
$$^{226}Ra\ \sigma\ (n,3n) = 0{\cdot}63 \pm 0{\cdot}07\ \text{barn}$$

THE $(n,2n)$ and $(n,3n)$ cross-sections of ^{226}Ra for 14·5 MeV neutrons were investigated as part of a general experimental study of the interaction of neutrons of this energy with some of the heavy elements. The $(n,3n)$ cross-section is in particular of some interest as it is practically the only $(n,3n)$ cross-section that it is possible to measure using the activation method for nuclides with masses greater than 210.

Three radioactive decay chains are present in a sample of radium after irradiation with 14·5 MeV neutrons. These are derived from the original ^{226}Ra, the $(n,2n)$ product ^{225}Ra, and the $(n,3n)$ product ^{224}Ra. In Table 1 a simplified version of these decay chains is given in which branching ratios of less than 1 per cent are omitted.

In order to determine the yields of ^{225}Ra and ^{224}Ra produced by the neutron irradiation, suitable nuclides had to be separated from their respective decay chains. These nuclides had to have convenient half-lives, and had to be recognizable in the presence of isotopes of the same element (and their daughters) present in the other decay chains.

The nuclide selected from the ^{225}Ra chain was ^{209}Pb, a β-particle emitter with a half-life of 3·3 hr. Bismuth was separated at first and then the ^{209}Pb was allowed to grow in from ^{213}Bi. Finally ^{209}Pb was separated and counted. The details of these separations together with the methods used to eliminate the activity of the lead isotopes in the other two chains are described in Section 2.3.

The yield of ^{224}Ra was estimated from the activity of ^{212}Po in its decay chain. This nuclide decays by α-particle emission and is in equilibrium with its parent ^{212}Bi which has a half-life of 60·5 min. Lead and bismuth were separated first from the irradiated radium and then ^{212}Bi together with ^{212}Po were separated from this fraction and counted. A more detailed description of the chemical separations and the resolution of the α-particle activity of ^{212}Po from that of other polonium and bismuth nuclides is given in Section 2.2.

TABLE 1

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At a late stage in these experiments it was pointed out to us[1] that ^{224}Ra occurs naturally in all samples of radium due to the presence of thorium impurities in the original uranium ore from which the radium was obtained (see Table 1). This natural content of ^{224}Ra in the radium samples used was measured and subtracted from the yields observed from the irradiated samples.

1. NEUTRON IRRADIATION

1.1. *Preparation of the radium sample*

Radium was irradiated as a solution of about 4 mg of the chloride in dilute HCl in a Perspex capsule. All operations involving the handling of radium were performed in a glove-box provided with local shielding. The capsule contained a cavity in the form of a shallow cylinder, with a diameter of 1·6 cm and a height of 0·15 cm. The cylindrical cavity in the capsule was filled exactly by means of a narrow channel which could be sealed externally. Care was taken to avoid air bubbles. After sealing, the capsule was removed from the glove-box and sealed in a double envelope of Saran film. This material was used to ensure the containment of radon from the radium solution. Finally, another envelope of P.V.C. film was added for mechanical protection.

1.2. *Determination of the neutron flux*

Fast neutrons were obtained by bombarding a tritiated zirconium target with 500 keV deuterons. The Perspex capsule was sandwiched between two thin aluminium disks which were positioned on the axis of the cylindrical hole containing the radium solution. This sandwich was then placed close to the back of the tritium target and irradiated for 6·6 hr.

The ^{27}Al$(n,\alpha)^{24}$Na reaction was used to monitor the neutron flux in this close position. In order to calibrate the ^{24}Na activity of the aluminium disks in terms of neutron flux a separate experiment was performed in which aluminium disks were irradiated in positions of known geometry with respect to a tritium target. The neutron output from this target was found by counting the associated α-particles from the (D,T) reaction in a known geometry and at an angle of 135° to the beam.

The difference in the neutron flux as recorded by the aluminium disks each side of the radium capsule was too great for a mean value to be assumed for the flux through the radium. A separate experiment with a similar capsule containing aluminium disks in place of the radium solution enabled a correction factor to this mean value to be calculated. The accuracy of the flux determined in this way was estimated to be ± 5 per cent. The magnitude of the flux through the radium solution was maintained at a level of 10^9 sec^{-1} cm^{-2} during the irradiation.

2. CHEMICAL SEPARATIONS

2.1. *Preliminary separation*

Before irradiation, the long-lived radium daughters ^{210}Pb, ^{210}Bi and ^{210}Po, were substantially removed by repeated cathodic depositions from a 2 N solution of HCl, using about 5 mg of inactive lead carrier for each electrolysis run. The details of the electrolysis are described in Section 2.5. Cathodic deposition of micro quantities of ^{212}Pb and ^{212}Bi from hydrochloric acid solutions of thorium salts has been described by HARRISON *et al.*[2]

The deposit from the first electrolysis was dissolved in concentrated HCl to provide a source of ^{210}Pb. After purification by anion exchange (see Section 2.5.3) this was used to determine the characteristics of the ion exchange columns used later and as a source of ^{210}Bi required as a tracer.

It was found that 95–100 per cent of lead, together with similar yields of bismuth and polonium were removed in each run. After about three runs, a final run was carried out, without the addition of fresh lead carrier, to remove any traces of inactive lead. The solution was then evaporated to dryness and the residue re-dissolved in about 0·3 ml of 1 N HCl for transfer to the irradiation capsule.

2.2. *Separations performed on the ^{224}Ra decay chain*

2.2.1. *Lead separation.* The irradiated solution was allowed to stand for 20 hr to enable ^{212}Pb to approach equilibrium with ^{224}Ra. An aliquot containing about 5 mg of inactive lead was added from

[1] Private communication (1959).
[2] A. D. R. HARRISON, A. J. LINDSAY and R. PHILLIPS, *Anal. Chim. Acta* **13**, 459 (1955).

a standard solution of lead chloride, and the solution was then electrolysed as already described, the mean time of deposition being noted. The electrode was removed and immediately weighed after washing with water and drying with alcohol. The deposit was dissolved by standing in hot concentrated HCl, and after again washing and drying, the electrode was re-weighed to give the weight of lead. The solution containing the active deposit was allowed to stand for about 5 hr to allow for the substantial decay of $^{214}Pb \rightarrow {}^{214}Bi \rightarrow {}^{214}Po$.

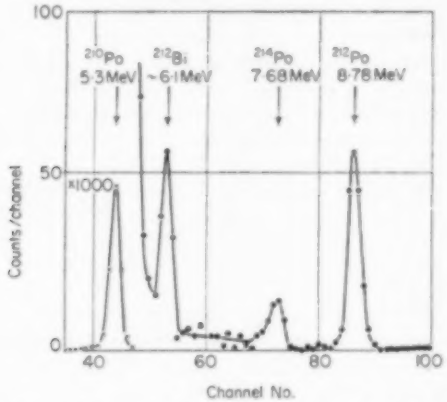

FIG. 1.—An α-particle energy spectrum of a bismuth source 3 hr after its extraction from a lead solution. The lead had previously been separated from a solution of ^{226}Ra which had been irradiated with 14·5 MeV neutrons.

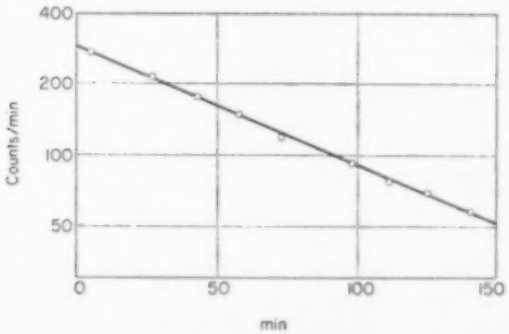

FIG. 2.—Decay of ^{212}Po in equilibrium with ^{212}Bi after separation from the decay chain of ^{224}Ra. ^{224}Ra was produced by the $^{226}Ra(n,3n)^{224}Ra$ reaction with 14·5 MeV neutrons.

2.2.2. *Bismuth separation.* Bismuth was then separated by deposition on platinum in a hydrogen atmosphere by a similar method to that described by ERBACHER[3]. Details are given in Section 2.5.2 of how the mean time of the deposition was noted and the α-particle energy spectrum (Fig. 1) of the deposit was measured using a gridded ionization chamber.

The peaks in the spectrum were due to ^{212}Bi (60·5 min), ^{212}Po (in equilibrium with ^{212}Bi), ^{214}Po (in equilibrium with 19·7 min ^{214}Bi), and ^{210}Po (138 day). The decay of the ^{212}Po 8·78 MeV α-particle peak is shown in Fig. 2. A source of ^{212}Bi and ^{212}Pb (standardized by means of a 4π proportional counter), was prepared from a ^{232}Th solution and used to find the efficiency of the ionization chamber.

2.2.3. *Yield of bismuth.* For the evaluation of the yield of bismuth, the disk and the solution from the deposition cell were assayed for 5 day ^{210}Bi which had grown in sufficient quantity in the ^{226}Ra solution in the interval between irradiation and electrolytic deposition. The disk was counted in a

[3] O. ERBACHER, *Naturwissenschaften* **20**, 391 (1932).

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Geiger counter through a 8 mg cm^{-2} aluminium absorber over a period of weeks to follow the decay of ^{210}Bi.

The ^{210}Bi in the solution from the deposition cell was also counted in this way after separation by anion exchange (see Section 2.5.3.). The conditions for this ion exchange separation and those used throughout these experiments were determined with a source of ^{210}Pb and ^{210}Bi using the data of KRAUS and NELSON[4].

2.2.4. *Correction for the preferential loss of bismuth.* With the high yields of lead and bismuth obtained in electrodeposition, the equilibria between the various species of lead and bismuth in the solution were virtually undisturbed by the electrolysis. However, during dissolution of the deposit from the electrode afterwards, lead was found to be dissolved preferentially. This had a negligible effect on the re-establishment of the equilibrium between ^{212}Bi (60·5 min) and ^{212}Pb, but could not be ignored in the measurement of the yield of bismuth involving the longer lived isotope ^{210}Bi.

To find the correction to the yield measurement, ^{210}Pb was separated by ion exchange from the solution in the cell after deposition of ^{212}Bi and measured by observing the growth of the ^{210}Bi activity. The observed ^{210}Bi activity of the deposition cell was then corrected by the amount calculated to have grown from ^{210}Pb in the interval between the deposition of bismuth and the ion exchange separation.

2.2.5. *Corrections for naturally occurring* ^{224}Ra. Two batches of radium of Belgian origin were used in these experiments and these were prepared, presumably free from any ^{228}Th, some 7 months before the $(n,3n)$ cross-section determinations were made. About 7 months after these determinations the natural ^{224}Ra content of these batches was measured using exactly the same procedures as used for the irradiated samples.

The natural ^{224}Ra content at the time of the cross-section determinations was then calculated taking into account the decay of ^{228}Ra and the growth of ^{228}Th. The corrections to the ^{224}Ra yields in the two cross-section determinations amounted to 59 and 58 per cent.

As the dates for the original separation of the batches of radium from the ore were not known, only lower limits for the ratio of ^{228}Th to uranium in the ore could be calculated. These amounted to $4{\cdot}2 \times 10^{-5}$ and $2{\cdot}6 \times 10^{-5}$ for the two batches. VON GUNTEN *et al.*[5] found that the thorium to uranium ratio in a sample of Belgian Congo ore was 44×10^{-5}.

2.3. *Separations performed on the* ^{225}Ra *decay chain*

2.3.1. *Bismuth separation.* This separation was carried out two to three weeks after irradiation to allow ^{225}Ac and its daughters to grow in. About 1 μC of ^{210}Bi, separated from the ^{210}Pb source, was used as a tracer to determine the yield in the separation. It was therefore necessary to reduce the ^{210}Pb and ^{210}Bi content of the ^{226}Ra solution to negligible proportions before the final separation of ^{213}Bi was performed and this was done by successive cathodic depositions as already described. To check the effectiveness of the removal of these two nuclides, the electrode from the last deposition was removed, washed and the deposit dissolved off in *aqua regia*. The solution of the deposit was then assayed by β-counting and was found to contain less than 0·002 μc of ^{210}Pb. The ^{226}Ra solution was allowed to stand for about 20 hr after the last electrolysis to re-establish the ^{225}Ac chain, during which time the estimated growth of ^{210}Pb was less than 0·003 μc.

The solution was then evaporated to dryness, re-dissolved in a small volume of 2 N HCl and transferred to a deposition cell for the electrochemical deposition of bismuth described earlier. In addition to the microgram quantity of bismuth carrier, a known aliquot of a ^{210}Bi solution containing about 1 μc of ^{210}Bi, 10–50 μg of platinum as a solution in hydrochloric acid and about 5 mg of $PbCl_2$, were also added to the solution. Hydrogen was then passed in a slow stream through the hot solution for half an hour to remove ^{222}Rn and thus reduce the level of 3 min ^{214}Po. Bismuth was then separated on a platinum disk as previously described. The disk although smooth at first became platinized as the separation proceeded and this was found to increase the yield of bismuth considerably. Deposition of tracer amounts of lead on a platinized surface had been found to be considerable but this was inhibited by the presence of milligram quantities of inactive lead.

[4] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Conf. Paper A/CONF/8P/837–USA. United Nations (1956).

[5] H. R. VON GUNTEN, W. BUSER and F. G. HOUTERMANS, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Conf. Paper A/CONF/15P/250. United Nations (1959).

After deposition and washing, the platinized deposit was dissolved off with *aqua regia* and the solution allowed to stand for about an hour to reduce the ^{210}Po activity to a negligible value.

2.3.2. *Lead separation.* The solution was then evaporated to dryness, fumed with concentrated HCl, and a fraction containing all the residual radium, ^{212}Pb, ^{210}Pb, ^{209}Pb and any traces of ^{214}Pb was separated by anion exchange and discarded. The source was left on the column for 1·5 hr to allow substantial decay of ^{213}Bi to ^{209}Pb and a second fraction containing all the ^{209}Pb so produced was separated (see Section 2.5.3.) The mean times of the two separations on the column were noted and the second fraction was evaporated to a low bulk and transferred quantitatively to a 20 μg cm^{-2} plastic film for counting in a 4π proportional counter.

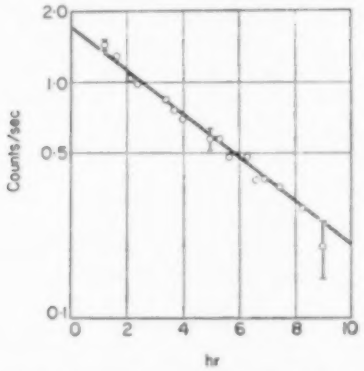

FIG. 3.—Decay of ^{209}Pb after separation from the decay chain of ^{225}Ra. ^{225}Ra was produced by the ^{226}Ra(n,2n)^{225}Ra reaction with 14·5 MeV neutrons.

The decay of the β-particle activity of ^{209}Pb isolated in such a second fraction is shown in Fig. 3. Activity from ^{210}Pb, derived from possible residual traces of ^{214}Bi, was not observed.

Another possible source of contamination was that from rhodium and silver isotopes produced by the decay of the ruthenium and palladium fission products of radium. The fission cross-section of ^{226}Ra for 14·5 MeV neutrons is, however, so small (NOBLES and LEACHMAN[6]) that contamination from this source could be neglected.

2.3.3. *Yield of bismuth.* A third fraction containing all the bismuth was finally separated, evaporated to low bulk and a known aliquot was counted for the decay of ^{210}Bi in a Geiger counter. The yield of bismuth was calculated from a comparison of this count with that of a known aliquot of the ^{210}Bi solution used to provide the tracer, both sets of counts being obtained in exactly similar conditions.

2.4 *Assay of* ^{226}Ra

The ^{226}Ra in the solution was assayed by suitable dilutions using volumetric glassware and calibrated micro-pipettes, aliquots being counted in the calibrated scintillation α-particle counter mentioned in Section 2.2.2. The maximum spread in results from several dilutions was 4 per cent. The purity of the sources was checked by observing the energy of the α-particle activity with a gridded ionization chamber.

2.5. *Details of chemical procedures*

2.5.1. *Cathodic deposition of lead and bismuth.* The depositions were carried out in an enclosed cell immersed in a water bath at a temperature of 70–75 °C. The anode and cathode wires were of 0·040 in. platinum fused through the glass lid of the cell. The lid was fitted to the cell by means of a B 34 ground glass joint and contained a vent-tube. The cathode, which was detachable, consisted of a $\frac{3}{4}$ in. square of platinum "unimesh" spotwelded to a short length of platinum wire. The cathode was attached to the cathode wire by a platinum sleeve and was arranged so that it almost touched the bottom of the cell, ensuring adequate stirring by convection. The anode wire was arranged to dip

[6] R. A. NOBLES and R. B. LEACHMAN, *Nucl. Phys.* **5**, 211 (1958).

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just below the surface of the solution, which was about 20 ml in volume. Electrolysis runs were continued for 20–30 min, with a starting potential of 4 V and a starting current of about 800 mA dropping to about 400 mA at the end of the run.

2.5.2. *Electrochemical separation of bismuth.* The solution was evaporated to dryness, the residue re-dissolved in a few ml of 2 N HCl, a few milligrams of inactive bismuth carrier added, and the solution transferred to a glass deposition cell, approximately 3·5 cm deep, 4 cm long and 1 cm wide. The cell was immersed in a hot water bath at a temperature of 80–90 °C and the volume of the solution adjusted to about 7 ml with 2 N HCl. A 1 in. platinum disk, previously cleaned and ignited, was mounted on a backing of polythene sheet by heating the polythene on a metal plate until it became plastic and then gently pressing the disk into the surface. A protective polythene ring was fitted over the edge of the disk and was welded to the backing by continuing to heat the plate. The assembly was removed from the metal plate, when cool, and placed in the solution with the back of the sheet against one side of the cell, so that about 80 per cent of the disk surface was immersed. The cell was covered with a polythene lid carrying a narrow-bore glass tube dipping to the bottom of the cell. Hydrogen was passed through the solution at a moderate rate for about 10 min. The disk assembly was then removed from the solution, washed repeatedly with water and then alcohol and, when dry, removed from the polythene with the aid of a hot knife blade. Any particles of polythene still adhering were removed by gently heating the disk.

2.5.3. *Ion exchange separations.* All separations were carried out with Amberlite XE 119 anion exchange resin, particle size $<50\ \mu$, using glass columns of internal diameter 0·4 cm.

Separation of bismuth from radium, lead and polonium

Evaporate to dryness, re-dissolve in small volume concentrated HCl, take a suitable aliquot.
Height of resin bed 3·5 cm; flow rate 0·2 ml/min; elute with concentrated HCl.
First fraction—4 ml. Contains all Ra and Pb.
Second fraction—14 ml. Contains all Bi.
Po and Pt remain on the column.

Separation of lead from radium, bismuth and polonium

Evaporate to dryness, re-dissolve in minimum volume of 1·5 M HCl.
Height of resin bed 10 cm; flow rate 0·3 ml/min; elute with 1·5 M HCl.
First fraction—5 ml. Contains all Ra.
Second fraction—15 ml. Contains all Pb.
Bi, Po and Pt remain on the column.

Separation of separate lead fractions from bismuth and polonium

Evaporate to dryness, re-dissolve in minimum volume of 6 M HCl.
Height of resin bed 4·0 cm; flow rate 0·2 ml/min.
First fraction—6 ml 6 M HCl. Contains all Ra and Pb.
Second fraction—3 ml 6 M HCl. Contains all Pb grown from Bi isotopes in the time interval.
Eluant contains 10 μg inactive Pb to inhibit adsorption losses.
Third fraction—15 ml concentrated HCl. Contains all Bi.
Po and Pt remain on the column.

3. RESULTS AND DISCUSSION

3.1. *Calculation and errors*

The cross-sections were calculated from the relation $\sigma = C/Nn$ where N is the number of ^{226}Ra atoms irradiated, n is the neutron flux, and C is the activity of the $(n,2n)$ or $(n,3n)$ product corrected for the finite time of irradiation.

The calculation of the ^{225}Ra activity produced involved the growth of ^{209}Pb from the separated ^{213}Bi and the growth and decay of ^{225}Ac formed by the decay of ^{225}Ra both during and after the irradiation. A similar calculation for the ^{224}Ra activity involved the growth and decay of ^{212}Pb formed by the decay chain of ^{224}Ra both

during and after the irradiation. Additional corrections were necessary in this case to take account of the transient equilibrium between ^{212}Bi and ^{212}Pb, the lower chemical yield of bismuth in the first ^{212}Pb, ^{212}Bi separation, and the loss of ^{212}Pb during this separation due to the loss of ^{220}Rn while the electrolysis was proceeding. These additional corrections did not total more than 12 per cent. The large correction for the naturally occurring ^{224}Ra content has already been discussed in Section 2.2.5.

The results of two separate determinations of both the $(n,2n)$ and $(n,3n)$ cross-sections for 14·5 ± 0·3 MeV neutrons are given as follows:

$$^{226}\text{Ra}\ \sigma\ (n,2n)\ \left.\begin{array}{l}\text{(i) } 1{\cdot}59 \pm 0{\cdot}26 \text{ barn}\\ \text{(ii) } 1{\cdot}61 \pm 0{\cdot}32 \text{ barn}\end{array}\right\} \text{ mean } 1{\cdot}6 \pm 0{\cdot}2 \text{ barn}$$

$$^{226}\text{Ra}\ \sigma\ (n,3n)\ \left.\begin{array}{l}\text{(i) } 0{\cdot}67 \pm 0{\cdot}11 \text{ barn}\\ \text{(ii) } 0{\cdot}60 \pm 0{\cdot}07 \text{ barn}\end{array}\right\} \text{ mean } 0{\cdot}63 \pm 0{\cdot}07 \text{ barn}$$

The standard deviation error quoted for the $(n,2n)$ cross-sections has been calculated from the individual errors for the weight of radium irradiated (3 per cent), the chemical yields (5 per cent), the neutron flux (5 per cent), the counting statistics (10 per cent), the counter efficiency measurements (2 per cent), and the separation time uncertainties (10 per cent). The corresponding individual errors for the $(n,3n)$ cross-sections were 3, 5, 5, 2, 1 and 1·5 per cent respectively. In this case however these errors will apply to both the determinations of the total yield of ^{224}Ra and that present naturally in the sample.

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3.2. *Discussion*

An approximate value of 2·75 barns for the total inelastic neutron cross-section for ^{226}Ra at this neutron energy can be inferred from the measured values for other heavy nuclides (McGregor *et al.*[7]). This cross-section is composed of the inelastic cross-section, the $(n,2n)$ and $(n,3n)$ cross-sections, and the fission cross-section. The fission cross-section has been measured by Nobles and Leachman[6] who obtained a value of 0·011 barn. A value of approximately 0·25 barn for the inelastic neutron cross-section can be deduced from a summary by Coon[8] of inelastic scattering experiments with other heavy nuclides.

Thus the combined total of the $(n,2n)$ and $(n,3n)$ cross-sections should be approximately 2·5 barns which is in fair agreement with the experimental total of 2·23 ± 0·25 barns.

[7] M. McGregor, W. P. Ball and R. Booth, *Phys. Rev.* **108**, 726 (1957).
[8] J. H. Coon, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Conf. paper A/CONF 15/P/666, p. 5. United Nations (1959).

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DECAY CHARACTERISTICS OF POTASSIUM-42 AND TELLURIUM-132*

C. GATROUSIS and C. E. CROUTHAMEL
Argonne National Laboratory
P.O. Box 299, Lemont, Illinois

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Abstract—The γ-spectra of potassium-42 and tellurium-132 have been examined with a sodium iodide crystal spectrometer. A recently reported 53 keV γ-transition has been observed in the decay of tellurium-132. Coincident summing in a single sodium iodide crystal at high geometry is used to reveal the main features of the relatively simple γ-decay schemes.

A LACK of complete γ-ray spectra for both tellurium-132 and potassium-42 has left the details of these γ-transitions in doubt. The features of the low intensity potassium-42 γ-transitions are difficult to observe because of the intense and very energetic β-emission. The tellurium-132 γ-transitions are also difficult to examine because of the rapid growth of the harder iodine-132 daughter activities. By using a large crystal, a multichannel analyser, and a simple coincident summing technique at high geometry, several additional features of the γ-transitions have been observed.

EXPERIMENTAL

A source of ^{42}K was prepared by a 10 min thermal neutron bombardment of natural potassium in the Argonne CP-5 reactor. The radiation was examined for a period of four days with the scintillation spectrometer. During this period, it was found that both the 1·52 MeV and 0·320 MeV γ-rays decayed with a 12·5 hr half-life.

Approximately 0·1 g of natural U_3O_8 was irradiated in the Argonne CP-5 reactor for a period of 8 hr. After allowing about 40 hr for the short-lived activities to decay, the tellurium was separated from the other fission products by the precipitation of elementary tellurium by reduction with SO_2 in a 3 M HCl solution. In order to verify the radiochemical purity of the isolated activity, tellurium was also separated chromatographically, and the sources prepared by both techniques were investigated. The following procedures illustrate both methods of separation.

The irradiated U_3O_8 was dissolved in a minimum of *aqua regia*, and after the addition of 10 mg tellurium carrier, the solution was evaporated to dryness with HBr three times in order to remove the nitrate ion and reduce tellurium to the 4+ valence state. Tellurium was then precipitated with SO_2 from a 3 M HCl solution. The precipitate was dissolved in 6 M HNO_3, and after destroying the nitrate ion with HCl evaporations, other contaminations were removed by an $Fe(OH)_3$ scavenge. Tellurium was finally precipitated from a hot 3 M HCl solution with SO_2, filtered on a glass-fibre disk, dried, and sandwiched between 5 mil Mylar film for counting.

The chromatographic method for the separation of tellurium activity from a fission product mixture has been described previously in detail.[1] A slight modification to this involved a preliminary SO_2 precipitation of tellurium from the other fission products. The precipitate was dissolved in a minimum of 6 M HNO_3, and this solution was applied to a strip of Whatman 3 MM chromatographic paper. The end of the strip was then immersed in an HF–methyl ethyl ketone solution, and this liquid was allowed to diffuse up the paper for a period of about 2 hr. After removing the paper strip from the solution and drying, the separated activities were located by the darkened spots which were

* Work performed under the auspices of the U.S. Atomic Energy Commission

[1] C. E. CROUTHAMEL and A. J. FUDGE, *J. Inorg. Nucl. Chem.* **5**, 240 (1958).

formed by placing the paper strip in contact with Kodak No-Screen X-ray film. The spot corresponding to the previously reported location of tellurium was cut out and mounted between two pieces of Mylar film.

The scintillation spectrometer in these studies consisted of a 4 in. by 4 in. diameter sodium iodide–thallium activated crystal mounted on a Dumont 6292 photomultiplier tube. The output of this photomultiplier was amplified and introduced into an Argonne model 256 channel pulse height analyser.

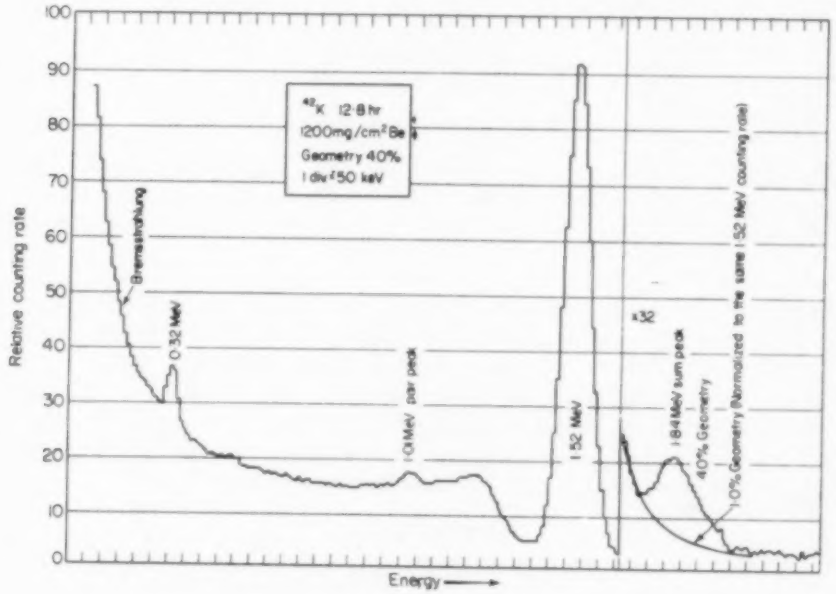

FIG. 1.

DISCUSSION AND RESULTS

Potassium-42

POHM *et al.*[2] in a recent study of ^{42}K β-ray line spectra, have identified two γ-transitions of 1·52 MeV and 0·320 MeV. These γ-rays have been observed directly with the sodium iodide scintillation crystal spectrometer. Use of the coincident summing technique in a single detector at high geometry shows clearly that the 1·52 MeV and 0·320 MeV γ-rays are in cascade (Fig. 1). The resulting 1·84 MeV sum peak at 40 per cent geometry is well above the high energy bremsstrahlung background radiation. The probability of summing both coincident 1·52 and 0·320 MeV γ-rays at 1·0 per cent geometry is extremely low, and no peak is observed above the bremsstrahlung background. It is also seen that, due to the high maximum energies of the two β-groups in the decay of ^{42}K, 3·545 MeV and 1·985 MeV, the intensity of external bremsstrahlung has practically obliterated the 0·320 MeV γ-ray. By use of beryllium absorbers, the intensity of external bremsstrahlung is kept to a minimum, and the 0·320 MeV peak is revealed clearly. Some of the 1·52 MeV photons also interact with the crystal by the pair production process, resulting in a 1·01 MeV annihilation photon escape peak (1·52–0·51 MeV) which appears in the γ-ray spectrum of ^{42}K.

[2] A. V. POHM, R. C. WADDELL and E. N. JENSEN, *Phys. Rev.* **101**, 1315 (1956).

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Tellurium-132

PAPPAS and CORYELL[3] have previously established the existence of a 0·230 MeV γ-ray in the decay of the fission product ^{132}Te. Also, NOVEY *et al.*[4] have reported γ-rays of 0·220 and 0·13 MeV in their study of this isotope. CHEEVER *et al.*[5] have recently reported a 53 keV γ-transition and computed *K*-shell conversion coefficients from coincidence data. In the present investigation a single large crystal has been used to observe the 0·053 MeV and 0·230 MeV γ-rays in cascade. The maximum energy of the β-transition reported is less than 0·3 MeV.

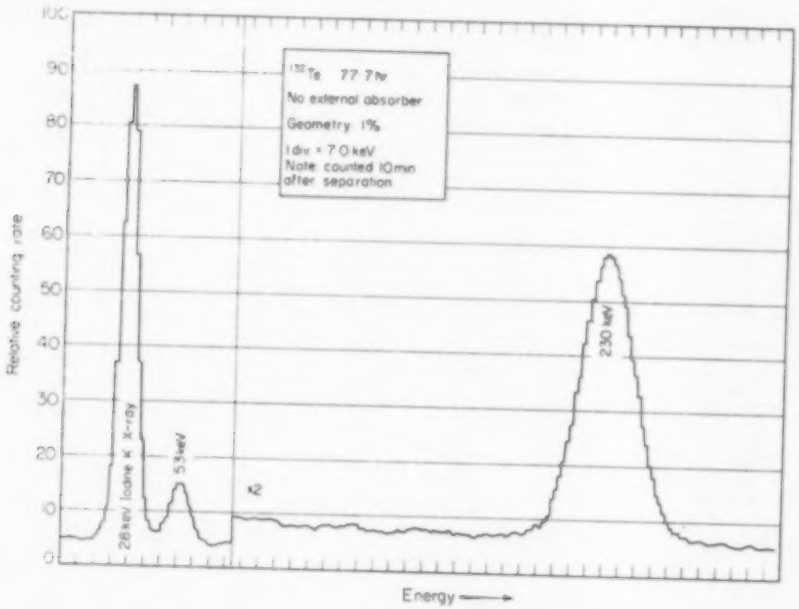

FIG. 2.

The γ-ray spectra obtained from the ^{132}Te separated by both techniques were identical. Fig. 2 represents the γ-ray spectrum of ^{132}Te, which was obtained at a geometry of 1 per cent within 10 min after separation. Because summing effects are not detectable at this low geometry, the previously reported 230 keV peak appears well resolved. More significantly, however, a 53 keV γ-transition is also exhibited, along with a very intense 28 keV iodine *K* X-ray. The spectrum shown in Fig. 3 was observed at a geometry of 48 per cent, the sample being placed directly on the 5 mil aluminium container of the crystal. The intense 28 keV iodine *K* X-ray and the 53 keV peak are still present in this spectrum, retaining the same relative ratios to each other, but not to the 230 keV gamma. The high energy side of the 230 keV γ-peak now appears extremely distorted, however, which indicates summing of 230 keV with both the 28 keV and 53 keV radiations.

[3] A. C. PAPPAS and C. D. CORYELL, *Phys. Rev.* **81**, 329A (1951).
[4] T. B. NOVEY, W. H. SULLIVAN, C. D. CORYELL, A. S. NEWTON, N. R. SLEIGHT and O. JOHNSON, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 958. McGraw-Hill, New York (1951).
[5] G. D. CHEEVER, W. S. KOSKI, D. R. TILLEY and L. MADANSKY, *Phys. Rev.* **110**, 922 (1958).

Iodine-132 has no highly converted gamma, and no γ-transition below 530 keV energy. The growth of ^{132}I daughter, therefore, had very little effect on the low energy ^{132}Te γ-spectrum. The low yields[6] or short half-lives of the other tellurium fission products result in a negligibly small background activity, due to these chemically inseparable isotopes.

The γ-ray spectra of ^{132}Te, which had been separated by both techniques described above, were studied for several days. These observations revealed that the ratio of

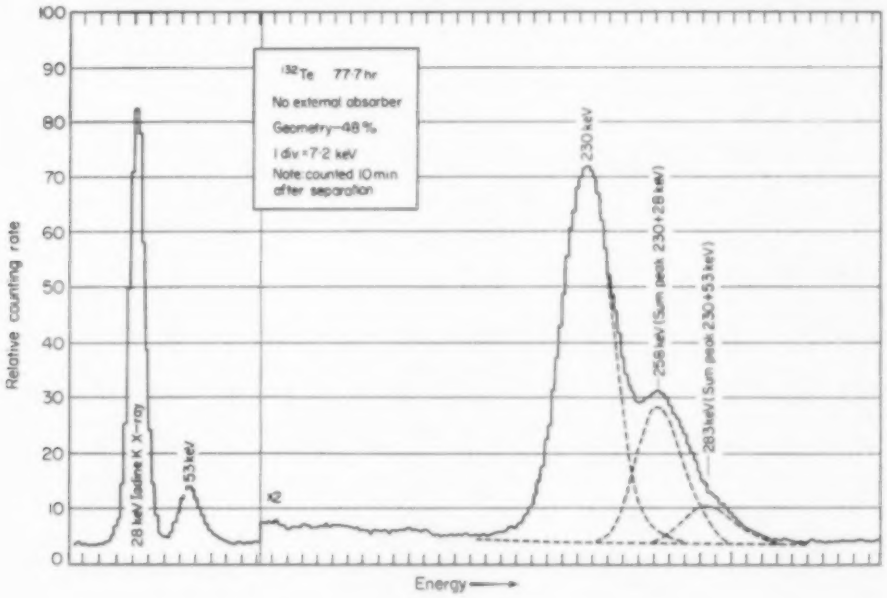

FIG. 3.

the 230 keV to 53 keV γ-ray remained constant during this period. Furthermore, both peaks decayed with a 77·7 hr half-life, characteristic of the isotope under investigation. Examination of spectra taken during growth of the 2·3 hr ^{132}I daughter activity revealed that no appreciable contribution was being made to the area under the ^{132}Te peaks which had been already identified.

The spectrum obtained at a counting geometry of 48 per cent, Fig. 3, indicates that the 53 keV transition is highly converted ($e_k/\gamma \sim 5$), and also that internal conversion of the 230 keV transition is relatively much lower. This is borne out by the absence of an 81 keV (53 + 28 keV) sum peak. The slight distortion of the 53 keV peak on the high energy side, however, gives some indication of summing between cascading 28 keV iodine K X-rays.

Although accurate K shell conversion coefficients for the two γ-transitions are extremely difficult to compute using the summing technique, some knowledge of the decay scheme characteristics is gained and previously reported data can be confirmed by this method. Coincident summing in a single sodium iodide crystal shows that the 230 keV γ-transition is in cascade with a 53 keV transition.

[6] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, A/CONF/8P/614, U.S.A. United Nations (1956).

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In order to compute the absolute intensities of the 28, 53 and 230 keV radiations it was necessary to correct the observed full energy peak counting rates for the overall detector efficiency. The X-ray attenuation coefficients of GRODSTEIN[7] were used to compute the point source intrinsic efficiency of the sodium iodide crystal and the full energy peak efficiency was then obtained from an experimentally determined peak

TABLE 1

Energy of radiation (keV)	Absolute intensity (arbitrary units)
28	110 ± 2
53	19 ± 0·6
230	100 ± 2

to total γ-ratio of selected monochromatic sources. AXEL's[8] escape peak calculations were used in computing the 53 keV full energy peak efficiency. The intensity of the 28 keV iodine K X-rays was then corrected for the contribution from the unresolvable 25 keV escape peak (53 minus 28 keV), and also for the small attenuation in the aluminium cover and light reflector surrounding the crystal. The K shell fluorescence yield was obtained from a smooth curve plotted with the data of BROYLES *et al.*[9] and GRAY[10].

The absolute intensities of each radiation computed in this manner are shown in Table 1. These results are in excellent agreement with the K shell conversion coefficients computed by CHEEVER *et al.* from coincidence data, $\alpha_k = 5{\cdot}35 \pm 0{\cdot}22$ for the 53 keV transition and $\alpha_k = 0{\cdot}05 \pm 0{\cdot}04$ for the 230 keV transition.

[7] G. W. GRODSTEIN, National Bureau of Standards, Circular 583 (1957).
[8] P. AXEL, *Rev. Sci. Instrum.* **25**, 391 (1954).
[9] C. D. BROYLES, D. A. THOMAS and S. K. HAYNES, *Phys. Rev.* **89**, 715 (1953).
[10] P. R. GRAY, *Phys. Rev.* **101**, 1306 (1956).

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 18 to 21. Pergamon Press Ltd. Printed in Northern Ireland

LIMITATIONS OF THE LIGAND SOLUBILITY METHOD FOR STUDYING COMPLEX FORMATION

H. S. ROSSOTTI
Department of Chemistry, University of Edinburgh, Scotland

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Abstract—The limitations inherent in the ligand solubility method for determining the stability constants of complexes of uncharged ligands are examined, and compared with the limitations of the metal salt solubility method. The ligand solubility method can only usefully be applied to the study of systems ML, M_2L, M_3L, . . . , in which no species contains more than one ligand, and is best used in cases where only the first complex, ML, is formed.

COMPLEX formation between a metal ion, M^{2+}, and a sparingly soluble uncharged ligand, L, is sometimes studied by measuring the solubility of the ligand in aqueous solutions containing different total concentrations, M, of metal ion.[1] The ionic strength of the solution is usually kept constant, and it is assumed that the activity coefficients of all species are independent of the detailed composition of the solution. The ligand solubility method has been used to study silver(I) complexes of unsaturated hydrocarbons[2–5] and of organic iodides,[6] and would be equally applicable to the study of metal ion complexes of sparingly soluble amines (e.g. phenanthroline). The addition of halogen molecules to a central halide ion has been studied analogously by measuring the solubility of halogen in solutions containing different total concentrations of halide ions.[7,8]

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In the general case where complexes M_qL_p ($1 \leqslant q \leqslant Q$, $1 \leqslant p \leqslant P$ and charges are omitted) are formed, the solubility of the ligand is given by

$$L = l + \sum_{1}^{Q}\sum_{1}^{P} p[M_qL_p] = S + \sum_{1}^{Q}\sum_{1}^{P} p\beta_{qp}m^qS^p \qquad (1)$$

where m and l are the free concentrations of metal ions and ligand molecules respectively, $\beta_{qp} = [M_qL_p]/m^ql^p$ is the overall stoicheiometric stability constant of M_qL_p for the appropriate ionic medium and temperature, and $S = l$ is the solubility of ligand (which is assumed to be mononuclear) in the absence of metal ions. A correction term must be added to equation (1) if any chemical reaction takes place between

[1] L. J. ANDREWS, *Chem. Rev.* **54**, 713 (1954).
[2] L. J. ANDREWS and R. M. KEEFER, *J. Amer. Chem. Soc.* **71**, 3644 (1949); **72**, 3113, 5304 (1950); **74**, 640 (1952).
[3] G. K. HELMKAMP, F. L. CARTER and H. J. LUCAS, *J. Amer. Chem. Soc.* **79**, 1306 (1957).
[4] R. E. KOFAHL and H. J. LUCAS, *J. Amer. Chem. Soc.* **76**, 3931 (1954).
[5] N. OGIMACHI, L. J. ANDREWS and R. M. KEEFER, *J. Amer. Chem. Soc.* **78**, 2210 (1956).
[6] L. J. ANDREWS and R. M. KEEFER, *J. Amer. Chem. Soc.* **73**, 5733 (1951).
[7] G. A. LINHART, *J. Amer. Chem. Soc.* **40**, 158 (1918).
[8] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN (Editors), *Stability Constants, Part II; Inorganic Ligands* pp. 109, 117, 123. Chemical Society, London (1958).

the ligand and the solvent species, e.g. the protonation of basic ligands, or the hydrolysis of halogens. Rearrangement of equation (1) gives

$$\frac{L-S}{mS} = \sum_{1}^{Q}\sum_{1}^{P} p\beta_{qp} m^{q-1} S^{p-1} \tag{2}$$

Previous workers have assumed that

$$M \gg \sum_{1}^{Q}\sum_{1}^{P} [M_q L_p] - [ML]$$

and have used the approximate relationship

$$m \sim M - L + S \tag{3}$$

Combination of equations (2) and (3) gives

$$\frac{L-S}{S(M-L+S)} = \sum_{1}^{N} n\beta_{1n} S^{n-1} + (M-L+S)\sum_{1}^{P} p\beta_{2p} S^{p-1} + \sum_{3}^{Q}\sum_{1}^{P} p\beta_{qp}(M-L+S)^{q-1} S^{p-1} \tag{4}$$

Thus, if only mononuclear complexes, $ML_n (1 \leqslant n \leqslant N)$, and dinuclear complexes, M_2L_p, are present, the left-hand side of equation (4) will be a linear function of $(M - L + S)$ provided that equation (3) is valid. Moreover, if ML and M_2L are the only complexes formed in appreciable concentrations, equation (4) reduces to

$$\frac{L-S}{S(M-L+S)} = \beta_{11} + \beta_{21}(M-L+S) \tag{5}$$

The stability constants of a number of silver(I) complexes have been obtained graphically using equation (5). If $[M_2L] \ll (m + [ML])$, preliminary values of β_{11} and β_{21} may be obtained by means of equation (5), and refined by successive approximations, using the relationships

$$m = M - \beta_{11} mS - 2\beta_{21} m^2 S \tag{6}$$

and

$$\frac{L-S}{mS} = \beta_{11} + \beta_{21} m \tag{7}$$

which are rigorous provided that ML and M_2L are the only complexes formed. Equations (5) and (7) reduce to

$$\frac{L-S}{S(M-L+S)} = \beta_{11} = \text{constant} \tag{8}$$

for systems in which only the species M, L and ML are present.

Since it is impossible to check the validity of equation (3) by the ligand solubility

method alone, the use of equation (5) is unjustified unless there is independent evidence of the nature of the species formed. For example, in mononuclear systems,

$$M - L + S = \frac{(L - S)(1 - \bar{n})}{\bar{n}} \tag{9}$$

where

$$\bar{n} = \frac{L - S}{M} \tag{10}$$

$$= \frac{\sum_{0}^{N} n\beta_{1n}l^n}{\sum_{0}^{N} \beta_{1n}l^n} \tag{11}$$

The term $(L - S)/S(M - L + S)$ is therefore more generally given by

$$\frac{L - S}{S(M - L + S)} = \frac{\bar{n}}{(1 - \bar{n})S} = \beta_{11} + \sum_{2}^{N} \frac{n - \bar{n}}{1 - \bar{n}} \beta_{1n}S^{n-1} \tag{12}$$

Since $S = l$ is constant in solutions which are saturated with ligand, $\bar{n}$ is also constant, and the saturated solutions are "corresponding".[9-11] Thus, the quantity $(L - S)/S(M - L + S)$ is constant for a mononuclear system, regardless of the number of complexes formed. Moreover, comparisons of equations (8) and (12) show that the former gives only an upper limit for the value of β_{11}. The magnitude of the error introduced by using equation (8) instead of equation (12) depends on the solubility of the ligand and on the stepwise stability constants of the complexes. If S, and hence $\bar{n}$, is very low, probably the only complexes which need be considered are ML and ML_2. In a system of this type the use of equation (8) is unjustified unless $2SK_2 \ll 1$, where $K_n = [ML_n]/[ML_{n-1}]l$ is the stepwise stoicheiometric stability constant of the species ML_n. This condition may well be fulfilled for silver(I) hydrocarbon complexes in aqueous solution as the ligands are sparingly soluble in water ($l \leqslant 0{\cdot}022$ M for aromatic hydrocarbons) and as K_1 would be expected to be considerably greater than K_2 for π-bonded complexes. However, higher free ligand concentrations are obtained using aqueous solutions of hydrocarbon derivatives ($l = 0{\cdot}06$ M for acetophenone[2]) or solutions of hydrocarbons in mixed aqueous-organic solvents ($l = 0{\cdot}63$ M for benzene in equimolar aqueous methanol[5]). Values of β_{11} obtained using equation (8) should therefore be treated with reserve until there is independent evidence that the concentration of ML_2 is negligible in these solutions.

If polynuclear species are present in solution, the value of

$$\{\beta_{11} + \sum_{2}^{N}(n - \bar{n})\beta_{1n}S^{n-1}/(1 - \bar{n})\}$$

may be obtained by extrapolating the plot of $(L - S)/S(M - L + S)$ against $(M - L + S)$ to zero total metal ion concentration. However, the use of equations (5) and (7) to calculate the value of β_{21} is again unjustified, unless it is

[9] J. BJERRUM, *Kgl. Danske Videnskab. Selskab Mat.-fys. Medd.* **21**, No. 4 (1944).
[10] S. FRONAEUS, *Acta Chem. Scand.* **5**, 139 (1951).
[11] H. IRVING and D. H. MELLOR, *J. Chem. Soc.* 3457 (1955).

certain that $p = 1$ for all complexes formed. Since equation (3) is valid for systems in which $q = p$, the relationship

$$\frac{L - S}{S(M - L + S)} = \text{constant} + 2\beta_{22}S(M - L + S) \tag{13}$$

could, in principle, be used to calculate the value of β_{22} for a system in which it were certain that M_2L_2 was the only polynuclear complex present.

The value of $\bar{n}$ for the mononuclear complexes may also be obtained[3] using equation (10). Since solutions saturated with ligand are corresponding,

$$\lim_{M \to 0} 0 \frac{dL}{dM} = \bar{n}$$

However, stability constants cannot be calculated from a single pair of values $\bar{n}$, S unless it is certain that only a given species is present.

The ligand solubility method is therefore of very limited applicability. Equations (5), (6), (7), (8) and (13) are only valid if it has been shown by independent measurements that not more than one ligand group is present in each complex. Moreover, values of individual stability constants cannot be calculated from the summation terms obtained using equations (4) and (12). These limitations arise from the fact that, although M, L and m can be varied, the free ligand concentration remains constant.

An analogous restriction arises in studying complex formation by measuring the solubility of a sparingly soluble metal salt, ML_c, in a solution containing ligand anions, L^{v-} ($z = cv$). Since the solubility product, $S_c = ml^c$ is constant, the free metal ion and ligand concentrations cannot be varied independently.[12,13] By analogy with equation (1), the solubility of ML_c is given by

$$M = \sum_0^Q \sum_0^P q[M_qL_p] = \sum_0^Q \sum_0^P q\beta_{qp}S_c{}^q l^{p-cq} \tag{14}$$

The coefficient of a given term l^t— in the power series (14) contains the stability constants β_{qp} of all species for which $p - cq = t$. For example, if $c = 2$, equation (14) may be expanded to

$$M = S_2l^{-2} + (\beta_{11}S_2 + 2\beta_{23}S_2{}^2 + 3\beta_{35}S_2{}^3 \ldots)l^{-1} + (\beta_{13}S_2 + 2\beta_{25}S_2{}^2 + 3\beta_{37}S_2{}^3 \ldots) + \ldots \tag{15}$$

and it is impossible to distinguish between the various complexes in the series ML, M_2L_3, M_3L_5, ..., or between those in the series ML_2, M_2L_4, M_3L_6, ..., from solubility data alone. Similarly, if $c = 1$ (i.e. if $z = v$) the coefficients of the terms l^0 and l are respectively $(\beta_{11}S_1 + 2\beta_{22}S_1{}^2 \ldots)$ and $(\beta_{12}S_1 + 2\beta_{23}S_1{}^2 \ldots)$, and, in this special case, it is impossible to distinguish between species of the same charge. Thus the metal salt solubility method cannot be used independently to determine stability constants for systems in which polynuclear complexes are formed. However, unlike the ligand solubility method, it can be successfully used for studying purely mononuclear systems.

Acknowledgement—I am most grateful to Dr. F. J. C. Rossotti for helpful discussions.

[12] I. Leden, *Svensk Kem. Tidskr.* **64**, 249 (1952); *Acta Chem. Scand.* **10**, 812 (1956).
[13] R. O. Nilsson, *Arkiv. Kemi* **12**, 219 (1958).

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THE FORCE CONSTANTS OF $Cr(CN)_6^{3-}$ AND $Cr(CO)_6$*

V. CAGLIOTI, G. SARTORI and C. FURLANI
Department of General and Inorganic Chemistry of the University of Rome, and
Department of Physical Chemistry of the University of Trieste

(*Received* 17 *June* 1959)

Abstract—The complete vibrational analysis of an octahedral molecule $Me(XY)_6$ is presented, together with its application to the spectra of $Cr(CO)_6$ and of $Cr(CN)_6^{3-}$, as a refinement of a previous treatment where each ligand group was regarded as a single point mass. With a potential function of the valence force type, the force constant of the stretching metal–carbon bond is greater for $Cr(CO)_6$ than for $Cr(CN)_6^{3-}$. A discussion of the assignment of the vibrational spectra of octahedral complex cyanides shows that, owing to intermixing of the symmetry co-ordinates in the normal modes and to perturbations due to lattice interactions, no simple direct relationship can be expected between the values of the fundamental frequencies and the metal–carbon bond character.

MANY papers have been published in recent years on the infra-red spectra of complex cyanides. If we limit our considerations to the octahedral complexes, we see that most preliminary studies have been based on a simplified model in which each of the CN-groups has been assigned a unique point mass of atomic weight 26. The vibrational problem is then reduced to that of a system consisting of seven masses with only six normal vibrations (A_{1g}, E_g, $2T_{1u}$, T_{2g}, T_{2u}). Such a model appears however to be sometimes too drastically simplified; if for instance we want to study the stretching motions Me—C, it happens that these give rise to frequencies close to those of other motions (e.g. the bending Me—C—N) which are not considered in the simplified model. The actual vibrations are therefore intermixed, and the simplified model, which considers only one of the two intermixing modes, becomes insufficient.† One must then take into consideration the actual molecular structure of the complex with all its atoms, and the vibrational analysis for an octahedral complex cyanide must be performed on the basis of a model of type $Me(AB)_6$ having thirteen distinct masses and thirteen normal vibrations (the number of the stretching and bending modes is doubled, and furthermore one of the rotations of MeX_6 becomes a vibration, T_{1g}).

We have performed such a calculation for the complex $Cr(CN)_6^{3-}$ on the ground of previously measured infra-red absorption data.[1] The potential function we have chosen is of the valence-force type, with four main force constants and ten interaction constants Table 1. The symmetry co-ordinates for the problem of thirteen masses are given in Table 2, and the *G*- and *F*-matrix elements in Table 3.

A thorough analysis of the infra-red spectrum of $Cr(CN)_6^{3-}$ permits the identification of the fundamental frequencies given in Table 4. Our assignments are supported by the analogous assignment proposed for the molecule $Cr(CO)_6$ by HAWKINS *et al.*[2] in their accurate work on the vibrational spectrum of the carbonyls of Cr and of Mo;

* Presented at the International Conference on Co-ordination Chemistry, London, April 6th–11th, 1959.
† This situation has been kindly pointed out to us by C. F. W. T. PISTORIUS (private communication).

[1] V. CAGLIOTI, G. SARTORI and M. SCROCCO, *R.C. Accad. Naz. Lincei* **22**, 266 (1957); **23**, 355 (1957); V. CAGLIOTI, G. SARTORI and C. FURLANI, *Ibid.* **25**, 260 (1958).
[2] N. J. HAWKINS, H. C. MATTRAW, W. W. SABOL and D. R. CARPENTER, *J. Chem. Phys.* **23**, 2422 (1955).

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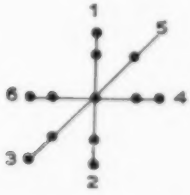
TABLE 1

$$2V = \sum_1^6 {}_x f_x \Delta x_i^2 + \sum_1^6 {}_y f_y \Delta y_i^2 + 2\sum_1^6 {}_{x_i \neq x_j} f_{xx} \Delta x_i \Delta x_j + 2\sum_1^6 {}_{y_i \neq y_j} f_{yy} \Delta y_i \Delta y_j$$
$$+ 2\sum_1^6 {}_{y_i,\ y_j} f_{xy} \Delta y_i \Delta y_j + 2\sum_1^6 {}_{x_i,y_i} f_{xy} \Delta x_i \Delta y_i + \sum_1^{12} {}_\alpha x^2 f_\alpha \Delta \alpha_i^2 + \sum_1^{12} {}_\beta x y f_\beta \Delta \beta_i^2$$
$$+ 2\sum_1^{12} {}_{\alpha_i \neq \alpha_j} x^2 f_{\alpha\alpha} \Delta \alpha_i \Delta \alpha_j + 2\sum_1^{12} {}_{\alpha_i \neq \alpha_j} x^2 f_{\alpha\alpha} \Delta \alpha_i \Delta \alpha_j + 2\sum_1^{12} {}_{\beta_i \neq \beta_j} x y f_{\beta\beta} \Delta \beta_i \Delta \beta_j$$
$$+ 2\sum_1^{12,12} {}_{\alpha_i,\beta_j} x^{\frac{1}{2}} y^{\frac{1}{2}} f_{\alpha\beta} \Delta \alpha_i \Delta \beta_j + 2\sum_1^{6,12} {}_{x_i,\alpha_j} x f_{x\alpha} \Delta x_i \Delta \alpha_j + 2\sum_1^{6,12} {}_{x_i,\beta_j} \sqrt{xy} f_{x\beta} \Delta x_i \Delta \beta_j$$

f_x = main force constant for the stretching Cr—C (x)
f_y = main force constant for the stretching C—N (y)
f_α = main force constant for the bending C—Cr—C (α)
f_β = main force constant for the bending Cr—C—N (β)

TABLE 2



A_{1g}: $S_1^x = \frac{1}{\sqrt{6}}(x_1 + x_2 + x_3 + x_4 + x_5 + x_6)$

$S_1^y = \frac{1}{\sqrt{6}}(y_1 + y_2 + y_3 + y_4 + y_5 + y_6)$

E_g: $S_1^x = \frac{1}{2}(x_3 - x_4 + x_5 - x_6)$

$S_2^y = \frac{1}{2}(y_3 - y_4 + y_5 - y_6)$

T_{1u}: $S_1^\beta = \frac{1}{2}(\beta 4_3 + \beta 5_6 + \beta 6_5 - \beta 3_4)$

T_{1u}: $S_1^x = \frac{1}{\sqrt{2}}(x_1 - x_2)$

$S_1^y = \frac{1}{\sqrt{2}}(y_1 - y_2)$

$S_1^z = \frac{1}{\sqrt{8}}(-z_{13} - z_{14} - z_{15} - z_{16} + z_{23} + z_{24} - z_{25} + z_{26})$

$S_2^\beta = \frac{1}{2}(-\beta 4_2 + \beta 5_1 + \beta 6_1 - \beta 3_2)$

T_{2g}: $S_1^\alpha = \frac{1}{2}(\alpha_{34} - \alpha_{36} - \alpha_{45} + \alpha_{56})$

$S_1^\beta = \frac{1}{2}(\beta 4_3 - \beta 5_6 + \beta 6_5 - \beta 3_4)$

T_{2u}: $S_1^z = \frac{1}{\sqrt{8}}(z_{13} - z_{14} + z_{15} - z_{16} - z_{23} + z_{24} - z_{25} + z_{26})$

$S_2^\beta = \frac{1}{2}(-\beta 4_2 - \beta 5_1 + \beta 6_1 + \beta 3_2)$

x = displacement of a distance Cr—C from the equilibrium value
y = displacement of a distance C—N from the equilibrium value
α = displacement of an angle C—Cr—C from the equilibrium value
β = displacement of an angle Cr—C—N from the equilibrium value

TABLE 3

A_{1g}:	$G_{xx} = \mu_C$	$G_{yy} = \mu_C + \mu_N$	$G_{xy} = -\mu_C$
E_g:	$G_{zz} = \mu_C$	$G_{ww} = \mu_C + \mu_N$	$G_{zw} = -\mu_C$
T_{1g}:	$G_{\beta\beta} = \frac{\mu_N}{y^2} + \mu_C\left(\frac{1}{x} + \frac{1}{y}\right)^2$		
T_{1u}:	$G_{zz} = 2\mu_{Cr} + \mu_C$	$G_{yy} = \mu_C + \mu_N$	$G_{xy} = -\mu_C$
	$G_{\alpha\alpha} = \frac{2\mu_C}{x^2} + \frac{8\mu_{Cr}}{x^2}$	$G_{\beta\beta} = \frac{\mu_N}{y^2} + \mu_C\left(\frac{1}{x} + \frac{1}{y}\right)^2 + \frac{4\mu_{Cr}}{x^2}$	
	$G_{\alpha\beta} = \sqrt{2}\left[\mu_C\left(\frac{1}{x^2} + \frac{1}{xy}\right) + 4\frac{\mu_{Cr}}{x^2}\right]$		
	$G_{z\alpha} = \frac{4\mu_{Cr}}{x}$	$G_{z\beta} = \frac{2\sqrt{2}\mu_{Cr}}{x}$	$G_{y\alpha} = G_{y\beta} = 0$
T_{2g}:	$G_{\alpha\alpha} = \frac{4\mu_C}{x^2}$	$G_{\beta\beta} = \frac{\mu_N}{y^2} + \mu_C\left(\frac{1}{y} + \frac{1}{x}\right)^2$	$G_{\alpha\beta} = 2\mu_C\left(\frac{1}{x^2} + \frac{1}{xy}\right)$
T_{2u}:	$G_{\alpha\alpha} = 2\frac{\mu_C}{x^2}$	$G_{\beta\beta} = \frac{\mu_N}{y^2} + \mu_C\left(\frac{1}{x} + \frac{1}{y}\right)^2$	$G_{\alpha\beta} = 2\mu_C\left(\frac{1}{x^2} + \frac{1}{xy}\right)$

A_{1g}:	$F_{zz} = f_z + 4f_{zz}$	$F_{ww} = f_w + f_{ww} + 4f_{ww}$	$F_{zw} = f_{zw}$
E_g:	$F_{zz} = f_z - 2f_{zz}$	$F_{ww} = f_w + f_{ww} - 2f_{ww}$	$F_{zw} = f_{zw}$
T_{1g}:	$F_{\beta\beta} = (f_\beta + 2f_{\beta\beta})xy$		
T_{1u}:	$F_{zz} = f_{zz}$	$F_{ww} = f_w - f_{ww}$	$F_{zw} = f_{zw}$
	$F_{\alpha\alpha} = (f_\alpha + 2f_{q\alpha\alpha})x^2$ $F_{z\alpha} = -x \cdot 2f_{z\alpha}$	$F_{\beta\beta} = (f_\beta + 2f_{\beta\beta})xy$ $F_{z\beta} = +\sqrt{(xy)} \cdot 2\sqrt{2}f_{z\beta}$	$F_{\alpha\beta} = -x^{\frac{1}{2}}y^{\frac{1}{2}}2f_{\alpha\beta}$ $F_{w\alpha} = F_{w\beta} = 0$
T_{2g}:	$F_{\alpha\alpha} = (f_\alpha - 2f_{\alpha\alpha})x^2$	$F_{\beta\beta} = xy(f_\beta - 2f_{\beta\beta})$	$F_{\alpha\beta} = -x^{\frac{1}{2}}y^{\frac{1}{2}}2f_{\alpha\beta}$
T_{2u}:	$F_{\alpha\alpha} = x^2(f_\alpha - 2f_{q\alpha\alpha})$	$F_{\beta\beta} = xy(f_\beta - 2f_{\beta\beta})$	$F_{\alpha\beta} = -x^{\frac{1}{2}}y^{\frac{1}{2}}\sqrt{2}f_{\alpha\beta}$

the only difference between our present assignment and the original proposals of HAWKINS lies in the frequencies after the two bending modes Me—C—O or Me—C—N ($\tilde{\nu}_{10}$ and $\tilde{\nu}_{12}$ of symmetry T_{2g} and T_{2u}), which should be 535 and 506 cm^{-1} for $Cr(CO)_6$ instead of 213 and 310 cm^{-1} a similar assignment, 598 and 570 cm^{-1}, has been proposed by MURATA and KAWAI.[3]

The force constants calculated according to the potential function in Table 1 are listed in Table 5.

The most interesting feature of the data quoted above is the significantly larger

[3] H. MURATA and K. KAWAI, *J. Chem. Phys.* **27**, 605 (1957).

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TABLE 4

Type	Repres.	Number	$Cr(CN)_6^{3-}$	$Cr(CO)_6$
Stretching Cr—C	A_{1g}	$\tilde{\nu}_2$	374	393
Stretching C—N or C—O	A_{1g}	$\tilde{\nu}_1$	2137	2108
Stretching Cr—C	E_g	$\tilde{\nu}_4$	336	373
Stretching C—N or C—O	E_g	$\tilde{\nu}_3$	2063	2019
Stretching Cr—C	T_{1u}	$\tilde{\nu}_5$	457	436
Stretching C—N or C—O	T_{1u}	$\tilde{\nu}_6$	2127	2000
Bending α	T_{1u}	$\tilde{\nu}_9$	124	102
Bending β	T_{1u}	$\tilde{\nu}_7$	694	661
Bending α	T_{2g}	$\tilde{\nu}_{11}$	106	90
Bending β	T_{2g}	$\tilde{\nu}_{10}$	536	535
Bending α	T_{2u}	$\tilde{\nu}_{12}$	95	80
Bending β	T_{2u}	$\tilde{\nu}_{12}$	496	506
Pseudo-rotation β	T_{1g}	$\tilde{\nu}_8$	536	539

TABLE 5.—FORCE CONSTANTS

	$Cr(CN)_6^{3-}$ (dynes/cm)	$Cr(CO)_6$ (dynes/cm)	Type
f_r	$+1{\cdot}9279 \times 10^5$	$+2{\cdot}5071 \times 10^5$	stretching Cr—C
f_R	$+16{\cdot}4223 \times 10^5$	$+15{\cdot}6496 \times 10^5$	stretching C—N or C—O
f_α	$+0{\cdot}1654 \times 10^5$	$+0{\cdot}1467 \times 10^5$	bending C—Cr—C
f_β	$+0{\cdot}2925 \times 10^5$	$+0{\cdot}3227 \times 10^5$	bending Cr—C—N or Cr—C—O
f_{rr}	$+0{\cdot}0731 \times 10^5$	$+0{\cdot}0448 \times 10^5$	interaction
f_{RR}	$+0{\cdot}1750 \times 10^5$	$+0{\cdot}2322 \times 10^5$	interaction
$f_{r_{cis}R}$	$-0{\cdot}3208 \times 10^5$	$+0{\cdot}4667 \times 10^5$	interaction
f_{rR}	$+0{\cdot}0620 \times 10^5$	$-0{\cdot}0046 \times 10^5$	interaction
$f_{\alpha\alpha}$	$+0{\cdot}0199 \times 10^5$	$+0{\cdot}0290 \times 10^5$	interaction
$f_{\varphi\alpha\alpha}$	$-0{\cdot}0017_3 \times 10^5$	$+0{\cdot}0119 \times 10^5$	interaction
$f_{\beta\beta}$	$+0{\cdot}0309 \times 10^5$	$+0{\cdot}0255 \times 10^5$	interaction
$f_{\alpha\beta}$	$-0{\cdot}0173 \times 10^5$	$-0{\cdot}0141 \times 10^5$	interaction
$f_{r\alpha}$	$-0{\cdot}0552 \times 10^5$	$-0{\cdot}0053 \times 10^5$	interaction
$f_{r\beta}$	$-0{\cdot}0036_6 \times 10^5$	$-0{\cdot}2458 \times 10^5$	interaction

(~30 per cent) value of the Cr—C stretching force constant in chromium carbonyl compared to that in chromium cyanide. Various factors may contribute to such a difference; among these we could possibly consider the different degree of double bond character between Cr and C in the two compounds, since Cr in $Cr(CO)_6$ has the electronic structure $(3d\varepsilon)^6$, i.e. it has the maximum number of electrons in the orbitals $3d\varepsilon$, which have symmetry T_{2g} (O_h) and are therefore adapted to forming π-bonds with the ligands, whereas in $Cr(CN)_6^{3-}$ chromium is only $(3d\varepsilon)^3$, so that the bond Cr—C presumably has less double bond character and is therefore weaker. Also, in

some other instances we can find a parallelism between frequency values and the strength of a bond deduced from the number of $d\varepsilon$ electrons, i.e. the degree of double bonding: for instance, the frequency $\tilde{\nu}_6$ (C—N stretching, T_{1u}) is found to increase in the series $Mn^{I}(CN)_6^{5-} < Mn^{II}(CN)_6^{4-} < Mn^{III}(CN)_6^{3-}$ with decreasing double-bond character between C and Me and with the consequent increase of triple bond character between C and N (see Table 6). The experimental values of stretching frequencies may not only be explicable on the basis of different degrees of π-bonding, and even a qualitative correlation is not always possible; thus, an increase or decrease in the frequency of a stretching mode may sometimes be explained in terms of more or less

TABLE 6

Complex	Structure	$\tilde{\nu}_8$ (~ stretching Me—C)	$\tilde{\nu}_6$ (stretching C—N) (main peak)
$Cr^{III}(CN)_6^{3-}$	$(d\varepsilon)^3$	457	2127
$Mn^{I}(CN)_6^{5-}$	$(d\varepsilon)^6$	—	2048
$Mn^{II}(CN)_6^{4-}$	$(d\varepsilon)^5$ (?)	—	2060
$Mn^{III}(CN)_6^{3-}$	$(d\varepsilon)^4$	443	2125
$Co^{III}(CN)_6^{3-}$	$(d\varepsilon)^6$	422	2088–2105–2129
$Fe^{II}(CN)_6^{4-}$	$(d\varepsilon)^6$	416	2041
$Fe^{III}(CN)_6^{3-}$	$(d\varepsilon)^5$	—	2125

intense π-bonding within a group of complex cyanides of the same metal in different oxidation states, but no such regularity is found among complex cyanides of different metals, and such comparisons are to be regarded as almost meaningless.

Some more general remarks are possible concerning the possibility of comparing the strengths of Me—C and C—N bonds in complex cyanides from the frequencies of the fundamental vibrations, whenever a complete vibrational analysis such as we have just described for $Cr(CN)_6^{3-}$ is not available:

(a) the frequencies usually attributed to C—N stretching (A_{1g} and E_g, Raman-active; T_{1u}, infra-red active) correspond effectively in most cases to nearly pure C—N stretching motions, because all Me—C stretching frequencies of the same kinds are much smaller and are therefore quite feebly intermixed; the valence-force treatment developed above for $Cr(CN)_6^{3-}$ shows however that fairly large values must be assumed for some C—N interaction force constants in order that the calculated frequencies may fit the experimental spectrum. Now, in the valence-force scheme, large interaction constants between non-adjacent bonds cannot have any real physical significance, and are to be regarded here rather as a formal device to account for the interactions between the CN^- ions and the surrounding crystal field. Therefore the measured frequencies account not only for the strength of the carbon–nitrogen bond, but also in part for some kind of lattice interactions.

(b) As to the Me—C stretching frequencies, it should be recalled that four fundamental modes belong to the type T_{1u}, which is active in the infra-red; of these four frequencies, the highest is a nearly pure C—N stretching and the lowest chiefly a C—Me—C bending, but the two intermediate frequencies ($\tilde{\nu}_7$ and $\tilde{\nu}_8$) both correspond to strongly intermixed motions arising from Me—C stretchings and Me—C—N bendings superposed to different extents. An approximate calculation shows that

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the displacements of the symmetry co-ordinates of bending Me—C—N and of stretching Me—C are for the frequency $\tilde{\nu}_7$ (694 cm^{-1}) of $Cr(CN)_6^{3-}$ in the ratio 38 : 62, while in $\tilde{\nu}_8$ (457 cm^{-1}) the ratio is about 18 : 82. Neither $\tilde{\nu}_7$ nor $\tilde{\nu}_8$ can therefore be chosen as a measure of the strength of the Me—C bond, because neither can be considered to represent a pure metal–carbon stretching motion.

As a result, if it is not possible to perform a complete vibrational analysis, we must be very cautious in attempting to draw conclusions regarding the strengths of Me—C or C—N bonds in a complex cyanide from a comparison of the observed frequency values of the fundamentals. Such a comparison will be of greater significance for the Me—C stretchings if it is made from the values of the Raman-active frequencies A_{1g} and E_g (which are not strongly intermixed) rather than from the infra-red-active frequency T_{1u}. Similarly, a comparison of the C—N stretching will be more reliable if made under conditions such that the effects of crystalline fields (which can in general vary from salt to salt) are eliminated or neutralized, i.e. again through the Raman-active frequencies A_{1g} or E_g as measured in aqueous solutions, where lattice interactions are replaced by solvation interactions, which are presumably of the same type for all octahedral complex cyanide anions.

It is therefore improbable that the experimentally measured values of the infra-red active frequencies of complex cyanides can be accounted for and correlated with the molecular structure in a simple way.

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MAGNETIC PROPERTIES AND CRYSTALLINE STRUCTURE OF AgO

J. A. McMillan*
Instituto de Física de San Carlos de Bariloche, Bariloche, Río Negro, Argentina

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Abstract—From the diamagnetic and crystalline behaviour, AgO is found to be not a true bivalent silver oxide but an Ag(I)–Ag(III) covalent oxide, crystallizing in the space group $P2_1/c$. The positions of the atoms are given and the covalent character of the Ag(III)–O and Ag(I)–O bondings is discussed.

Silver oxide, AgO, has had the attention of many workers since the days it was believed to be a peroxide, prior to the clarifying work of Barbieri[1]. Recently, interest has increased because AgO is the product of the oxidation of silver anodes in the so-called silver peroxide alkaline cells.[2,3] Its X-ray diffraction pattern has been used for its identification[4] (see Fig. 1). The first attempt to determine its crystalline structure was done by the author in 1954[5] finding a monoclinic lattice belonging to the space group $C2/c$–C_{2h}^6 with the positions Ag(4*d*), O(4*e*).[6] More recently, Graff and Stadelmaier[7] and Scatturin *et al.*[8] have reached the same results, the latter independently of the author's former ones. Nevertheless, the choice of such a space group involves the assumption of four bivalent silver ions per unit cell. If it were so, the oxide should be paramagnetic since Ag(II) has one unpaired electron. According to Neiding and Kazarnovskii[9], however, the oxide is diamagnetic, its susceptibility being $\chi = -0{\cdot}155 \times 10^{-6}$ emu/g. These authors have also found that AgO is a semiconductor with a positive temperature coefficient between −40°C and 20°C and an electrical conductivity at 17°C of 0·07 mho/cm, determined on powdered samples pressed at 12000 kg/cm².

AgO not only appears during the electrolytic oxidation of silver anodes in alkaline media[7,10] but also during the chemical oxidation of monovalent silver solutions in analogous conditions.[11] It seems doubtful, however, whether the same oxide appears during the electrolytic oxidation of silver anodes in acid media.[4] Probably silver oxisalts of the type $(Ag_3O_4)_2Ag(I)An$ (where An stands for a monovalent anion like nitrate, fluoride, perchlorate or acid sulphate) are produced in this process.[12]

AgO is stable in water up to 100°C and slightly unstable in alkaline solutions[13] giving rise to Ag_2O and oxygen. It dissolves in strongly acidified media yielding Ag(II)

* Present address: Argonne National Laboratory, Lemont, Illinois, spending the duration of a Guggenheim Fellowship.

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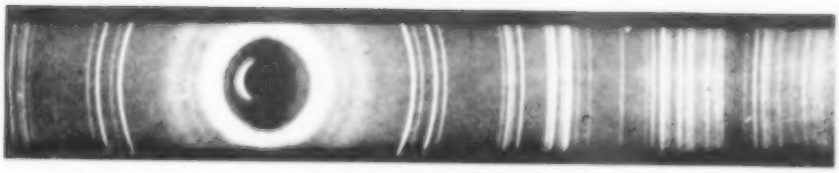

FIG. 1.—X-ray diffraction pattern of AgO.

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in solution whose paramagnetism corresponds closely to the one expected from spin contribution only.[9] The same value for the paramagnetism has been found in many co-ordinated solid compounds of divalent silver[14,15] that are, therefore, magnetically dilute.

EXPERIMENTAL RESULTS AND DISCUSSION

As previously stated, a true bivalent silver oxide should exhibit paramagnetism, which is not the case for AgO. NEIDING and KAZARNOVSKII[9] tried to explain the diamagnetism by assuming either a metallic bonding of silvers or a covalent bonding between two Ag(II) pairing the unpaired electrons and ionic bonding with oxygens. These hypotheses, however, are hard to accept since the metallic bonding should lead to much higher values of the conductivity and the Ag(II)–Ag(II) covalent bonding involves close linking between two small-radius dipositive kernels. It seems doubtful whether such a bonding could overcome the repulsive electrostatic potential, although this type of bonding has also been assumed in the case of the dark green diamagnetic Cu(II) derivative of diazoaminobenzene.[16] Otherwise, our results as well as those of SCATTURIN *et al.* indicate that silver ions are located in a face centred lattice which gives for the separation between neighbouring silver ions a value of 3·28 Å. This result, obtained assuming all silvers to be equivalent, is still valid if two Ag(III) are arranged in (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$) and two Ag(I) in ($\frac{1}{2}$, $\frac{1}{2}$, 0; $\frac{1}{2}$, 0, $\frac{1}{2}$) instead of arranging four Ag(II) in (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0). The relative differences between atomic scattering factors of the three kinds of silver ions are low. This change imposes a lower symmetry space group, namely $P2_1/c$–C_{2h}^5. The positions of the oxygens, however, remain undetermined. It should be noted in this respect that the former structure[5,8] leads to distances apart between oxygens of about 1·75 Å. The ionic radius of O^{2-} being 1·32 Å, this distance should be at least 2·64 Å. Since the compound is diamagnetic, Ag(III) can only be present if there is co-ordinated filling of one *d*-orbital. This can be done by resorting to hybridization with two of four atoms, namely: *dp* (linear), *ds* (angular), dsp^2 (square planar) or dp^3 (irregular tetrahedral). From these, *dp* and dsp^2 are the only ones that are compatible with the structure due to the planar arrangement of oxygens in this space group. Hybridization dsp^2 (or better *dp* plus *sp*), in addition, accounts for the bonding in the (011) plane. Accepting the latter hybridization, the positions of oxygens are approximately settled. It should be noted that the high density of the compound restricts the election of the oxygen parameters. The general positions for the oxygens being (x, y, z; $\bar{x}$, $\bar{y}$, $\bar{z}$; $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; x, $\frac{1}{2}-y$, $\frac{1}{2}+z$), this latter fact leads to $x \cong \frac{3}{4}$, $y \cong z \cong \frac{1}{4}$. Otherwise, from the standpoint of scattering, this arrangement is substantially equivalent to that chosen formerly.[5,8] The positions of the atoms are then:

AgO	$P2_1/c$–C_{2h}^5	$Z = 4$	
$a = 5{\cdot}85$ Å;	$b = 3{\cdot}48$ Å;	$c = 5{\cdot}50$ Å;	$\beta = 107°30'$
Ag(III)	$2a(\bar{1})$	0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$.	
Ag(I)	$2d(\bar{1})$	$\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0.	
O	4e(1)	$\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{3}{4}$; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$; $\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4}$.	

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Fig. 2 shows the lattice of AgO.

The following separations between neighbouring ions are obtained:

Ag(III)–O $\simeq$ Ag(I)–O $\simeq$ 2·1 Å, in agreement with the value found in the case of Ag_2O for the distance Ag(I)–O = 2·06 Å,

O–O $\simeq$ 2·8 Å $>$ 2·64 Å,

Ag(III)–Ag(III) = Ag(I)–Ag(I) = 3·28 Å, and

Ag(III)–Ag(I) = 3·39 Å.

Tripositive silver ions are then co-ordinated with four oxygens, two of them being closer (*dp*). From the four oxygens of the unit cell, two of them are the nearest

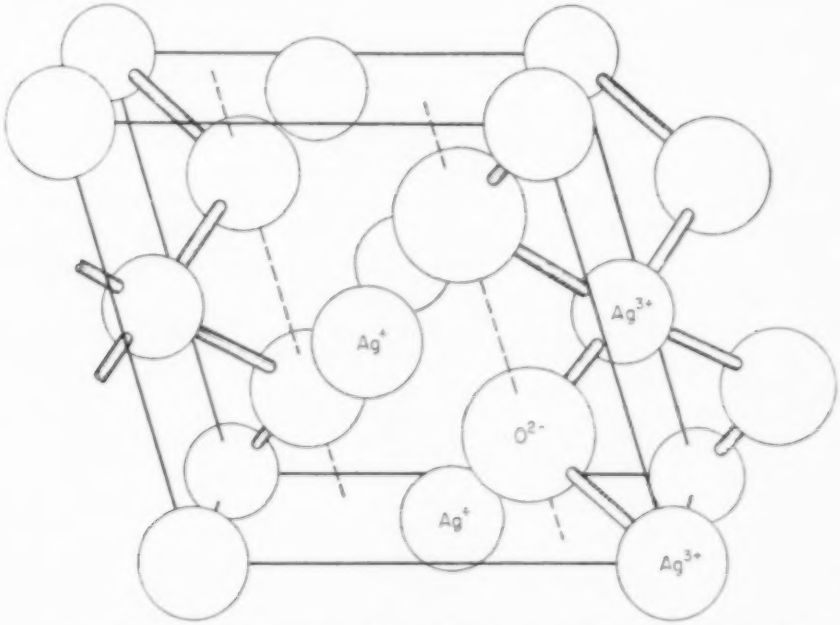

FIG. 2.—Arrangement of atoms in AgO. Only a few co-ordination bondings are shown to avoid complexity in the figure.

neighbours of each Ag(I) ion. This suggests a linear *sp*-co-ordination as is usual in monovalent silver covalent compounds. The deep blackness of AgO, in addition, can be attributed to the Ag–O bondings since, according to HELMHOLTZ and LEVINE[17], the greater the covalent character of the Ag–O bonding, the deeper the colour of the compound.

With respect to its property of semiconductivity, it should be emphasized that the value of the electrical conductivity is low and could be explained on the basis of an excess- or defect-oxygen lattice. There are, however, no experimental results to support this or any other assumption.

Further verification of the structure is very difficult since it has not been possible to obtain a single crystal of AgO but only finely divided powder samples.

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SUMMARY

The compound AgO crystallizes in the space group $P2_1/c$–C_{2h}^5. It is not a true bivalent silver oxide but an oxide of silver(I) and silver(III). Trivalent silver ions are coördinated with oxygens filling one *d*-orbital, being, therefore, diamagnetic. Monovalent silver ions are *sp*-co-ordinated with two oxygens. The property of semiconductivity of AgO can be attributed to an excess- or defect-oxygen lattice.

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DIVALENT THULIUM. THULIUM DI-IODIDE*

L. B. ASPREY and F. H. KRUSE
University of California Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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Abstract—The preparation and identification of a divalent thulium compound, TmI_2, is reported. Lattice constants for the hexagonal structures of TmI_2 and YbI_2 are: TmI_2, $a_0 = 4{\cdot}520 \pm 0{\cdot}003$ Å, $c_0 = 6{\cdot}967 \pm 0{\cdot}006$ Å; and of YbI_2, $a_0 = 4{\cdot}503 \pm 0{\cdot}003$ Å, $c_0 = 6{\cdot}972 \pm 0{\cdot}004$ Å.

AMONG the lanthanide elements in the trivalent state, three electronic configurations are especially stable: La(III), with the xenon configuration; Gd(III), with a half-filled 4*f* orbital; and Lu(III), with a completely filled 4*f* orbital.[1] The existence of stable divalent europium and ytterbium is explained as they have the Gd(III) and Lu(III) electronic structives respectively. The same argument has been extended to explain the existence of Sm(II) and, by analogy, a stable divalent thulium state might be expected. Some inconclusive evidence for the possible divalency of thulium has been reported.[2]

This paper reports the preparation and identification of the compound, TmI_2. Two methods of preparation of the compound are given. The X-ray powder data reported show conclusively the existence of a compound of hexagonal structure which is iso-structural with YbI_2 and therefore must be TmI_2. The chemical behaviour of the compound which supports this conclusion is discussed. X-ray data on YbI_2 are given which supplement and refine that given by DÖLL and KLEMM with a slight change in their reported lattice constants.[3]

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The thulium metal used in these experiments was reported to contain less than 1 per cent by weight of other rare earths. Spectrographic analysis at this laboratory indicated that 0·1 per cent calcium and 0·05 per cent magnesium were the only impurities detectable. The ytterbium metal used was reported to be 99+ per cent pure in regard to other rare earths and showed no detectable heavy rare earths. All other reagents were of reagent grade and were used without further purification other than oven drying.

The thulium di-iodide was prepared by two different methods, both of which used thulium metal as the reducing agent. In the first method, a clean, weighed piece of thulium metal was placed in a quartz tube. A compacted piece of mercuric iodide was added, just sufficient to convert all of the thullium metal to thulium di-iodide.[4] The HgI_2 was positioned so that it could be vacuum-sublimed without contacting the thulium metal. After sublimation of the mercuric iodide, the quartz tube containing the thulium metal and the mercuric iodide was sealed off at a pressure of $<10^{-4}$ mm of mercury. The sealed-off quartz tube was placed in an oven at 300°–400° for several days. After this time, the distinctive colour of the mercuric iodide had disappeared and the thulium metal had corroded.

* This work was sponsored by the U.S. Atomic Energy Commission.

[1] D. M. YOST, H. RUSSELL, JR. and C. S. GARNER, *The Rare Earth Elements and Their Compounds* pp. 4–6. John Wiley, New York (1947).
[2] D. M. YOST, H. RUSSELL, JR. and C. S. GARNER, *The Rare Earth Elements and Their Compounds* pp. 10–11. John Wiley, New York (1947).
[3] W. DÖLL and W. KLEMM, *Z. Anorg. Chem.* **241**, 239 (1939).
[4] R. J. CLARK, E. GRISWOLD and J. KLEINBERG, *J. Amer. Chem. Soc.* **80**, 4764 (1958).

The mercury metal formed in the reaction was then sublimed to the opposite end of the tube from the thulium and the tube sealed off. Mercury was recovered quantitatively. The remaining portion of the quartz tube containing the corroded thulium piece was again placed in an oven at 500°–600° for about a week. After this time, the tube was removed to a helium-filled dry box where it was opened. The original metal piece was now a dark coloured mass. This material was crushed and ground in a mortar and X-ray capillary specimens were prepared.

In the second method, thulium tri-iodide was prepared by vacuum drying of evaporated thulium iodide–hydrogen iodide solutions followed by heating at 400° *in vacuo*. The system was filled with helium and a clean piece of thulium metal was rapidly added to a section of the tube separated by a constriction from the TmI_3, followed by evacuation of the system to $<10^{-6}$ mm of mercury. The quartz tube was sealed off and placed in an oven at ~550° for one week. During this time, TmI_3 sublimed and reacted with the thulium metal. X-ray samples were prepared in a helium dry-box as in the first method.

Ytterbium di-iodide was prepared both as in the second method and also by thermal decomposition of YbI_3 followed by sublimation of the YbI_2 at about 750° *in vacuo*. This sublimation technique gave a product almost completely free of ytterbium oxy-iodide contamination but with over-large crystals causing a somewhat spotty powder pattern.

Preparation of pure TmOI was carried out by heating evaporated TmI_3 in air containing water-vapour. X-ray powder data were obtained in order to correct for the TmOI occurring in the TmI_3 preparations.

All X-ray photographs were obtained with a unit using filtered copper radiation. The powder camera was a 114·6 mm diameter Debye–Scherrer commercial unit. Type AA Eastman film was used.

RESULTS AND DISCUSSION

The X-ray powder patterns of the TmI_2 prepared by the two methods showed about forty lines, including high angle lines, which could be ascribed to a hexagonal cell with $a_0 = 4{\cdot}520 \pm 0{\cdot}003$ Å and $c_0 = 6{\cdot}967 \pm 0{\cdot}006$ Å. The values obtained for YbI_2 were $a_0 = 4{\cdot}503 \pm 0{\cdot}003$ Å and $c_0 = 6{\cdot}972 \pm 0{\cdot}004$ Å. Thus the unit cell for TmI_2 is slightly larger than for YbI_2, as might be expected from the lanthanide contraction. The $\sin^2\theta$ and intensity values for TmI_2 and YbI_2 from this study along with the values of DÖLL and KLEMM for YbI_2 are given in Table 1.[3]

The chemical observations supplement the structure data. In all cases, the dark coloured material showing this hexagonal TmI_2 phase was found to be very reactive. Upon contact with ordinary air containing water–vapour, small bubbles could be seen forming on the surface. It reacted very vigorously with water with the evolution of gas. It reacted more slowly with methyl alcohol with gas evolution and decolourized a solution of iodine in methyl alcohol. In one instance, where water was added rapidly to about two-tenths of a gramme of the salt, a fleeting violet-red colour was observed.

The quantitative nature of the X-ray data along with the supporting qualitative chemical observations is sufficient to prove the existence of the compound, TmI_2, and thus the divalency of thulium.

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TABLE 1.—X-RAY POWDER DATA, TmI_2, YbI_2 (CuK_α: $\lambda = 1{\cdot}5418$ Å)

TmI_2 ($a_0 = 4{\cdot}520$ Å, $c_0 = 6{\cdot}967$ Å)					TmOI**		YbI_2 ($a_0 = 4{\cdot}503$ Å, $c_0 = 6{\cdot}972$ Å)			
hkl	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	$I_{calc.}$*	$I_{obs.}$†	$\sin^2\theta$, obs.	$I_{obs.}$†	$\sin^2\theta$, calc.	$\sin^2\theta$, obs.	$I_{calc.}$* DÖLL KLEMM	$I_{obs.}$†
001	0·0122	0·0123	9	*m*−			0·0122	0·0123		*m*−
100	0·0388		1				0·0391	0·0389		*w*−
002	0·0490		2				0·0489	0·0502		*vw*
101	0·0510	0·0516	100	*vs*			0·0513	0·0510	100	*vs*
102	0·0878	0·0883	92	*s*	0·0868	*w*	0·0880	0·0889	61	*s*−
003	0·1102	0·1108	5	*vw*			0·1100	0·1115		*w*−
110	0·1163	0·1169	83	*s*	0·1140	*mw*	0·1172	0·1166	42	*s*
111	0·1285	0·1290	26	*w*			0·1294	0·1288	12	*w*+
103	0·1490	0·1492	59	*m*+			0·1491	0·1474	24	*m*−
200	0·1551		1		0·1581	*ms*	0·1563			
112	0·1653		5	*m*+			0·1661	0·1648		*w*−
201	0·1673	0·1680	57				0·1685	0·1680	20	*m*+
004	0·1958	0·1967	20	*m*−	0·1926	*ms*	0·1956	0·1975	6	*w*
202	0·2041	0·2046	56	*m*			0·2052	0·2047	16	*m*−
113	0·2265	0·2259	17	*m* + *B*	0·2256	*s*	0·2272	0·2261	5	*m*−
104	0·2346		1				0·2347			
203	0·2653	0·2658	41	*w*−			0·2663	0·2645	9	*w*
210	0·2715	0·2724	1	*vvw*			0·2735			
211	0·2837	0·2843	77	*m*−			0·2857	0·2850	16	*m*
005	0·3060		2	*wB*	0·3109	*w*	0·3056	0·3109		
114	0·3121	0·3130	85		0·3153	*mw*	0·3128	0·3148	17	*w*−
212	0·3205	0·3211	81	*w*+	0·3213	*vw*	0·3224	0·3215	15	*w*+
105	0·3448	0·3452	34	*w*			0·3447	0·3460		*m*−
300	0·3490	0·3496	38	*w*			0·3517	0·3510		*w*+
204	0·3509		1				0·3519			
301	0·3612	0·3610	6	*vvw*			0·3639	0·3634		*vw*
213	0·3817	0·3820	64	*w* + *B*	0·3823	*mw*	0·3835	0·3819		*w*
302	0·3980		3				0·4006	0·3993		*w*−
115	0·4223		12				0·4228			
006	0·4406		<½				0·4401	0·4422		*w*−
303	0·4592	0·4600	6	*vw*			0·4617	0·4622		*w*−
205	0·4611		54				0·4619			
220	0·4654	0·4660	34	*vw*	0·4679	*vw*	0·4689	0·4672		*w*−
214	0·4673		2				0·4691			
106	0·4794	0·4798	34	*vw*+			0·4792	0·4805		*w*+
221	0·4776		11				0·4811			
310	0·5041		1		0·5063	*mw*	0·5080			
222	0·5144	0·5165	2	*w*−			0·5178	0·5188		*w*+
311	0·5163		59				0·5202			
304	0·5448		69		0·5429	*ms*	0·5473	0·5458		*w*
312	0·5531	0·5528	68	*w* − *B*			0·5569	0·5560		*w*
116	0·5569		2				0·5573			
223	0·5756	0·5775	11	*w* − *B*	0·5732	*mw*	0·5789	0·5799		*w*
215	0·5775		61				0·5791			

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TABLE 1—(*continued*)

TmI_2 (a_0 = 4·520 Å, c_0 = 6·967 Å)					TmOI**		YbI_2 (a_0 = 4·503 Å, c_0 = 6·972 Å)			
hkl	$\sin^2\theta$, calc.	$\sin^2\theta$, obs.	$I_{calc.}$*	$I_{obs.}$†	$\sin^2\theta$, obs.	$I_{obs.}$†	$\sin^2\theta$, calc.	$\sin^2\theta$, obs.	$I_{calc.}$* DÖLL KLEMM	$I_{obs.}$†
206	0·5957	0·5953		*vvw*			0·5964			
007	0·5998						0·5991	0·5988		*w*
313	0·6143	0·6138		*w*—			0·6180	0·6167		*w*—
401	0·6327						0·6374	0·6387		*w*+
107‡	0·6375	0·6373		*vvw*			0·6382			
224	0·6612	0·6612		*vw*			0·6634‡	0·6636		*vw*
402	0·6695	0·6694		*vvw*			0·7136	0·7143		*vw*
216‡	0·7109	0·7120		*vw*			0·7554	0·7552		*w*—
403‡	0·7295	0·7300		*vw*						
008‡	0·7821						0·7811‡	0·7825		*w*—
321‡	0·7479	0·7475		*vw*						
207‡	0·7537	0·7515		*vw*						
315‡	0·8089	0·8086		*vvw*			0·8123‡	0·8122		*vw*
410‡	0·8131	0·8135		*vw*						
323‡	0·8457	0·8453		*vvw*			0·8510‡	0·8511		*vvw*
217‡	0·8698	0·8702		*vvw*			0·8711‡	0·8713		*w*
118‡	0·8983						0·8981‡	0·8985		*w*+
413‡	0·9231	0·9240		*vvw*			0·9291‡	0·9288		*vw*
405‡	0·9250									
316‡	0·9433	0·9429		*vw*			0·9466‡	0·9461		*w*—

* Normalized to 100 for the strongest line, CdI_2 structure assumed.
† Symbols for observed intensity: *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *B*, broad.
‡ Calculated and observed CuK_{α_1}: λ = 1·5405 Å.
** Interfering lines and intensities, not indexed.

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 36 to 43. Pergamon Press Ltd. Printed in Northern Ireland

SUBSTITUTION REACTIONS OF PLATINUM(IV) COMPLEXES

THE SYNTHESIS AND PROPERTIES OF *TRANS*-DITHIOCYANATO-BIS-(ETHYLENEDIAMINE)PLATINUM(IV) SALTS

R. C. JOHNSON and F. BASOLO
Department of Chemistry, Northwestern University, Evanston, Illinois

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Abstract—Substitution reactions of *trans*-$Pt(en)_2Cl_2^{2+}$ with several different reagents are reported. A description is given of what is believed to be the first synthesis of *trans*-$Pt(en)_2(SCN)_2^{2+}$ salts. The properties and possible structure of this complex are discussed.

PLATINUM(IV) ammine complexes containing other ligands in addition to ammonia or amine often are prepared by the oxidation of the appropriate platinum(II) ammine compound.[1] However, in some cases the desired platinum(IV) compound has been made by the replacement of one or more of its ligands by other groups. Recent studies suggest that these substitution reactions perhaps involve catalytic amounts of platinum(II) and proceed *via* a bridged, Pt(IV)–X–Pt(II) intermediate.[2] This paper reports the relative effectiveness of different X groups and makes use of this information to prepare certain complexes of platinum(IV). The complex *trans*-$Pt(en)_2(SCN)_2^{2+}$ is of particular interest. It had been reported by GROSSMANN and SCHÜCK[3] but was perhaps not prepared by them.

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Relative reactivities of different reagents. The method used to determine the relative reactivities of different reagents towards *trans*-$Pt(en)_2Cl_2^{2+}$ was essentially the same as that employed earlier in the studies of chloride exchange.[2] The symmetrical intermediate

$$\begin{array}{ccccc} & en & & en & \\ Cl & -Pt- & Cl & -Pt- & Cl \\ & en & & en & \end{array}$$

proposed for the $Pt(en)_2^{2+}$ catalysis of exchange in the system *trans*-$Pt(en)_2Cl_2^{2+}$—Cl^- requires that Pt(IV)–Pt(II) exchange at the same rate. This was demonstrated by using carbon-14 ethylenediamine[4]

$$Pt(^*en)_2^{2+} + \textit{trans}\text{-}Pt(en)_2Cl_2^{2+} \rightleftharpoons \textit{trans}\text{-}Pt(^*en)_2Cl_2^{2+} + Pt(en)_2^{2+} \quad (1)$$

and also by using L-propylenediamine.

$$Pt(en)_3^{2+} + \textit{trans}\text{-}Pt(1\text{-}pn)_2Cl_2^{2+} \rightleftharpoons Pt(1\text{-}pn)_3^{2+} + \textit{trans}\text{-}Pt(en)_2Cl_2^{2+} \quad (2)$$

Since the optical rotation at the sodium *D* line of *trans*-$Pt(1\text{-}pn)_2Cl_2^{2+}$ is approximately three times that of $Pt(1\text{-}pn)_3^{2+}$ the rate of equilibration (2) is readily determined by polarimetric measurements.

[1] *Gmelin's Handbuch der Anorganischen Chemie* Vol. 68, p. 486–610. Verlag Chemie (1957).
[2] F. BASOLO, A. F. MESSING, P. H. WILKS, R. G. WILKINS and R. G. PEARSON, *J. Inorg. Nucl. Chem.* **6**, 161 (1958); **8**, 203 (1958).
[3] H. GROSSMANN and B. SCHÜCK, *Ber. Dtsch. Chem. Ges.* **39**, 1896 (1906).
[4] R. G. WILKINS, Private communication.

Substitution reactions by such a mechanism as this also requires platinum exchange so that the relative rates of exchange were determined by the technique of using L-propylenediamine. Thus, the replacement of the chloro groups and the accompanying platinum exchange are believed to occur by the following scheme:

$$Pt(1\text{-}pn)_3^{2+} + X^- \overset{\text{fast}}{\rightleftharpoons} Pt(1\text{-}pn)_3X^+ \tag{3}$$

$$\begin{matrix} en \\ Cl\text{—}Pt\text{—}Cl^{2+} \\ en \end{matrix} + \begin{matrix} 1\text{-}pn \\ Pt\text{—}X^+ \\ 1\text{-}pn \end{matrix} \overset{\text{slow}}{\rightleftharpoons} \begin{matrix} en & & 1\text{-}pn \\ Cl\text{—}Pt\text{—}Cl\text{—}Pt\text{—}X^{2+} \\ en & & 1\text{-}pn \end{matrix} \overset{\text{slow}}{\rightleftharpoons} \begin{matrix} en \\ Cl\text{—}Pt^+ \\ en \end{matrix} + \begin{matrix} 1\text{-}pn \\ Cl\text{—}Pt\text{—}X^{2+} \\ 1\text{-}pn \end{matrix} \tag{4}$$

$$Pt(en)_2Cl^+ + X^- \overset{\text{fast}}{\rightleftharpoons} Pt(en)_2X^+ + Cl^- \tag{5}$$

$$\begin{matrix} 1\text{-}pn \\ Cl\text{—}Pt\text{—}X^{2+} \\ 1\text{-}pn \end{matrix} + \begin{matrix} en \\ Pt\text{—}X^+ \\ en \end{matrix} \overset{\text{slow}}{\rightleftharpoons} \begin{matrix} 1\text{-}pn & & en \\ Cl\text{—}Pt\text{—}X\text{—}Pt\text{—}X^{2+} \\ 1\text{-}pn & & en \end{matrix} \overset{\text{slow}}{\rightleftharpoons} \begin{matrix} 1\text{-}pn \\ Cl\text{—}Pt^+ \\ 1\text{-}pn \end{matrix} + \begin{matrix} en \\ X\text{—}Pt\text{—}X^{2+} \\ en \end{matrix} \tag{6}$$

The half-lives for the change in optical rotation of reaction mixtures starting with $Pt(1\text{-}pn)_3^{2+}$, *trans*-$Pt(en)_2Cl_2^{2+}$ and X^- at room temperature (~25°C) are given in Table 1.

TABLE 1.—THE EFFECT OF X^- ON THE RATE OF Pt(II)–Pt(IV) EXCHANGE IN THE SYSTEM $Pt(1\text{-}pn)_3^{2+} + trans\text{-}Pt(en)_2Cl_2^{2+} + 2X^- \rightleftharpoons trans\text{-}Pt(1\text{-}pn)_2X_2^{2+} + Pt(en)_3^{2+} + 2Cl^-$ AT ROOM TEMPERATURE (~25°C) AND USING 0·0137 M $[Pt(1\text{-}pn)_3](ClO_4)_2$ AND 0·0148 M *trans*-$Pt(en)_2Cl_2](ClO_4)_2$

X^-	$[X^-]$ (M)	$t_{\frac{1}{2}}$ (min)	X^-	$[X^-]$ (M)	$t_{\frac{1}{2}}$ (hr)
Br^-	0·020	<3	OH^-	0·037	1†
CNS^-	0·025	<3	SO_4^{2-}	0·014	1
CN^-	0·031	<3	ClO_4^-	0·056	4
Cl^-	0·026	3	$C_2H_3O_2^-$	0·024	4
CNO^-	0·020	15	F^-	0·036	4
NO_2^-	0·029	20	NO_3^-	0·029	4

† The optical rotation of this alkaline solution at first increases and then decreases almost to its original value. It has been observed that under these conditions there is reduction of the platinum(IV) complex. A detailed study is being made of the reaction between platinum(IV) complexes and hydroxide ion and this will be reported in a later publication.

Syntheses and attempted syntheses of platinum(IV) complexes. The data in Table 1 suggests that those reagents causing equilibration with a half-life of less than 1 hr might well be found to replace the co-ordinated chloro groups and yield *trans*-$Pt(en)_2X_2^{2+}$. These data also indicate that the chloro groups are perhaps not replaced by the less reactive reagents. This has been amply confirmed by isolating the products from reaction mixtures containing *trans*-$Pt(en)_2Cl_2^{2+}$, X^- and catalytic amounts of $Pt(en)_2^{2+}$. Earlier work had shown that nitrite ion can replace chloride[5] and also that *trans*-$Pt(en)_2Br_2^{2+}$ reacts with HCl in the dark only in the presence of catalytic amounts of $Pt(en)_2^{2+}$.[6]

The procedure used to study all of these systems was essentially the same in every case. In general, a solution containing 0·5 g (0·001 moles) of *trans*-$[Pt(en)_2Cl_2]Cl_2$, catalytic amounts (0·005 g) of $[Pt(en)_2]Cl_2$, 0·1 moles of HX (or MX) and a minimum amount of water was allowed to stand at room temperature in the diffuse light of the laboratory for as long as 24 hr. If it appeared that no reaction had occurred during this time then the mixture was placed on the steam bath for a few hours.

[5] P. H. WILKS, Thesis, Northwestern University (1957).
[6] A. F. MESSING, Thesis, Northwestern University (1957).

In some cases the crystalline product separated from the aqueous reaction mixture. Whenever crystals did not separate, sufficient alcohol and ether were added to precipitate the reaction product.

Details of the reaction between *trans*-$[Pt(en)_2Cl_2]Cl_2$ and HBr will serve to illustrate the experimental method used. A reaction mixture containing 0·62 g of *trans*-$[Pt(en)_2Cl_2]Cl_2$ and 12 ml of 48% HBr was heated on a steam bath for 1 hr. A small amount (0·006 g) of $[Pt(en)_2]Cl_2$ had been previously added to act as a catalyst. The mixture was then cooled in an ice bath and excess ethanol was added to precipitate the bright yellow crystalline product. The salt was collected on a filter, washed with alcohol and ether, then air dried at 100° to weight 0·83 g (95 per cent yield). (Found: Pt, 31·0; Br, 50·6. Calc. for $[Pt(en)_2Br_2]Br_2$: Pt, 30·7; Br, 50·4%).

TABLE 2.—PRODUCTS ISOLATED FROM REACTION MIXTURES OF *trans*-$[Pt(en)_2Cl_2]Cl_2$ + HX (or MX)

X^-	Reaction product	Remarks
HBr	*trans*-$[Pt(en)_2Br_2]Br_2$	see text
KCNS	*trans*-$[Pt(en)_2(SCN)_2](CNS)_2$	see text
KCN	*trans*-$[Pt(en)_2(CN)(OH)](NO_3)_2$	†
HCl	*trans*-$[Pt(en)_2BrCl]Cl_2$ from $[Pt(en)_2Br_2]Br_2$	ref. 6
KCNO	it was not possible to isolate a product.	
$NaNO_2$	*trans*-$[Pt(en)_2(NO_2)_2](NO_3)_2$	ref. 5
NaOH	some reduction to $Pt(en)_2^{2+}$	see Table 1
$NaSO_4$	*trans*-$[Pt(en)_2Cl_2]SO_4$	no reaction
$HClO_4$	*trans*-$[Pt(en)_2Cl_2](ClO_4)_2$	no reaction
$HC_2H_3O_2$	*trans*-$[Pt(en)_2Cl_2](C_2H_3O_2)_2$	no reaction
NaF	*trans*-$[Pt(en)_2Cl_2]Cl_2$	no reaction
HNO_3	*trans*-$[Pt(en)_2Cl_2](NO_3)_2$	no reaction

† The reaction between *trans*-$[Pt(en)_2Cl_2]Cl_2$ and KCN yields a yellow precipitate. This precipitate was dissolved in a minimum amount of dilute nitric acid. Addition of excess concentrated nitric acid and acetone gave the designated nitrate salt.

This product is believed to be the *trans* isomer because it has the same ultra-violet and infra-red spectrum as does the compound prepared by the reaction of $Pt(en)_2^{2+}$ with Br_2. Likewise, the complex is readily reduced to $Pt(en)_2^{2+}$, a property characteristic of *trans*-$PtA_4X_2^{2+}$ complexes.

The above reaction was duplicated but this time no $Pt(en)_2^{2+}$ was added as a catalyst. In this case the product isolated in approximately 90 per cent yield showed that the co-ordinated chloro groups had not been replaced. (Found: Pt, 34·5; Br, 29·3; Cl, 11·8. Calc. for $[Pt(en)_2Cl_2]Br_2 \cdot H_2O$: Pt, 34·6; Br, 28·4; Cl, 12·6%).

This experiment along with similar observations by MESSING indicates that catalytic amounts of $Pt(en)_2^{2+}$ are necessary to get substitution at these experimental conditions. MESSING also observed that certain preparations of *trans*-$[Pt(en)_2Cl_2]Cl_2$ contain sufficient catalyst to promote reaction. In such cases, the reaction did not take place if the Pt(IV) solution was first allowed to react with Ce(IV). This is believed to oxidize the Pt(II) catalyst.

The results of similar studies for the reaction of *trans*-$[Pt(en)_2Cl_2]Cl_2$ with other reagents are summarized in Table 2.

Synthesis and properties of trans-$[Pt(en)_2(SCN)_2]^{2+}$ *salts.* A solution of 2·0 g of *trans*-$[Pt(en)_2Cl_2]Cl_2$ in 10 ml of water was mixed with a solution of 25 g of KCNS in 25 ml of water at room temperature. Yellow crystals began to separate from solution almost immediately. These crystals were collected on a suction filter and washed with a minimum amount of ice-water. After air drying at room temperature, the salt weighed 2·2 g (88 per cent yield). The same result was obtained when the reaction was carried out in the dark room instead of the diffuse light of the laboratory. (Found: Pt, 34·64; CNS^- (ionic), 22·5; CNS^- (total), 41·2; C, 17·10; H, 3·27. Calc. for $[Pt(en)_2(SCN)_2](CNS)_2 \cdot H_2O$: Pt 34·5; CNS^- (ionic), 20·5; CNS^- (total), 41·0; C, 17·0; H, 3·18%).

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The reaction was repeated but before the addition of KCNS, the solution of *trans*-$[Pt(en)_2Cl_2]Cl_2$ was allowed to react with enough Ce(IV) to oxidize any catalytic amount of $Pt(en)_2^{2+}$. Under these conditions the reaction gave about the same results as described above. The fact that Ce(IV) does not prevent the formation of $[Pt(en)_2(SCN)_2](CNS)_2$ would indicate that the reaction need not be catalysed by Pt(II) and may proceed by some mechanism other than the bridged mechanism. Alternatively, it might be that catalytic amounts of $Pt(en)_2^{2+}$ are readily generated by the reduction of *trans*-$Pt(en)_2Cl_2^{2+}$ by CNS^-, as is described later. In an attempt to establish whether or not this reaction is subject to Pt(II) catalysis, semi-quantitative spectrophotometric studies were made. The change in optical density at 420 mμ was observed as a function of time for three similar reaction

TABLE 3.†—EFFECT OF $Pt(en)_2^{2+}$ AND OF Ce(IV) ON THE RATE OF THE REACTION *trans*-$[Pt(en)_2Cl_2](NO_3)_2$ + 4 KCNS → $[Pt(en)_2(SCN)_2](CNS)_2$ + 2 KNO_3 + 2 KCl

	Optical densities at 420 mμ‡		
Time (min)	Reactants only	Added $Pt(en)_2^{2+}$	Added Ce(IV)
0	0·00	0·00	0·00
0·25	0·12	1·3	0·00
1·0	0·44	1·3	0·00
2·0	0·96	1·3	0·01
3·0	1·3	—	0·01
5·0	1·3	—	0·01
26·0	—	—	0·04
55·0	—	—	0·34
65·0	—	—	0·44
170·0	—	—	1·3

† Experimental conditions: 0·020 g *trans*-$[Pt(en)_2Cl_2](NO_3)_2$, 0·20 g KCNS; 0·0025 g $[Pt(en)_2]Cl_2$; 0·0025 g $Ce(HSO_4)_4$; 7 ml 1 M H_2SO_4; 25°C
‡ Optical density of these reaction mixtures at infinite time is 1·3.

mixtures: one containing only the reactants, another containing the same concentration of reactants plus a small amount of Pt(II) and a third containing reactants plus Ce(IV). The results obtained are summarized in Table 3.

Nitrate and perchlorate salts of $Pt(en)_2(SCN)_2^{2+}$ were also prepared. The nitrate salt was obtained by adding an excess of cold concentrated nitric acid to a saturated solution of $[Pt(en)_2(SCN)_2](CNS)_2 \cdot H_2O$ surrounded by an ice–salt bath. Yellow crystals of $[Pt(en)_2(SCN)_2](NO_3)_2$ separated almost immediately. A saturated solution of this salt when treated with an excess of concentrated perchloric acid gave the corresponding perchlorate. (Found: Pt 34·7; CNS^-, 20·7. Calc. for $[Pt(en)_2(SCN)_2](NO_3)_2$: Pt, 35·1; CNS^-, 20·9%) and (Found: CNS^-, 17·0. Calc. for $[Pt(en)_2(SCN)_2](ClO_4)_2$: CNS^-, 18·4%).

The slightly low CNS^- content is perhaps due to some hydrolysis of the dithiocyanato complex. All Pt analyses were done by the ignition of the complex. This does not work for perchlorate salts which tend to explode on ignition. The nitrate and perchlorate salts were also identified by comparing their spectrum with that of the parent compound and by their ease of reduction to $Pt(en)_2^{2+}$.

A similar attempt was made to prepare the chloride and bromide salts by treating *trans*-$[Pt(en)_2(SCN)_2](CNS)_2$ with HCl and HBr respectively. Instead the salts isolated were *trans*-$[Pt(en)_2Cl_2]Cl_2$ and *trans*-$[Pt(en)_2(Br_2)]Br_2$, which shows that the co-ordinated thiocyanate is rather easily replaced.

The solid nitrate and perchlorate salts of $Pt(en)_2(SCN)_2^{2+}$ are stable in the air at room temperature whereas the thiocyanate salt gradually decomposes over a period of two weeks to a brownish coloured

tar. An aqueous solution containing 0·30 g of $[Pt(en)_2(SCN)_2](CNS)_2 \cdot H_2O$ in 20 ml of water on standing at room temperature slowly (14 days) yields 0·10 g of a red crystalline material. Analysis of this material indicates that there has been some reduction to Pt(II) and some loss of ethylenediamine. Both the analysis and the red colour suggest it is a bridged polymer of Pt(II) and Pt(IV) of the type

$$\begin{matrix} & & \text{en} & & \text{en} & & \text{en} \\ -\text{NCS}- & \text{Pt} & -\text{NCS} & \left[-\text{Pt}- \right. & \text{NCS} & \left. \right]_n -\text{Pt}- & \text{NCS}- \\ & (\text{SCN})_2 & & & (\text{SCN})_2 & & (\text{SCN})_2 \end{matrix}$$

(Found: Pt, 43·9; C, 14·4; H, 2·32. Calc. for Pten$(SCN)_3$: Pt, 45·5; C, 14·0; H, 1·87. Calc. for $Pt_3(en)_3(SCN)_{10}$: Pt, 43·5, C, 14·2; H, 1·79%). No attempt was made to determine the structure of this red crystalline material. However, its Pt analysis is in better agreement with a trimeric structure containing two Pt(IV) and one Pt(II) than with an infinite chain structure of alternating Pt(IV) and Pt(II). The same red product separates from a solution of the nitrate salt under the same conditions. In both cases the original solutions have a pH of 2·6 and the final solution a pH of 1·3. The final solution also gives a test for SO_4^{2-} showing that some of the CNS^- was oxidized.

The reduction of $[Pt(en)_2(SCN)_2](NO_3)_2$ with SO_2 gave an 80% yield of $[Pt(en)_2]Cl_2$ when precipitated by the addition of HCl and alcohol.

GROSSMANN and SCHÜCK reported the synthesis of $[Pt(en)_2(SCN)_2](CNS)_2$ by the reaction of $K_2Pt(SCN)_6$ with ethylenediamine. However, unlike the compound described above, their compound was insoluble in water and mineral acids and soluble only in *aqua regia*. It was felt that this was a different isomer of the same complex and several attempts were made to prepare the compound by the method of GROSSMANN and SCHÜCK. Since they did not give detailed directions, the conditions of temperature and concentration were varied in different experiments but always similar results were obtained. In a typical preparation 1·05 g of $K_2[Pt(SCN)_6]$ was dissolved in 25 ml of water heated to 50°. To this warm solution was then added 0·25 ml of ethylenediamine. A pale yellow product separated and was collected. In most cases products having different colours and Pt content separated from the solution in stages. In all cases the Pt content of the products was much higher than that of $[Pt(en)_2(SCN)_2](SCN)_2$. The chief product in all of the preparations was a Pt(II) complex with the composition $Pt(en)(SCN)_2$. (Found: Pt, 52·0; C, 13·17; H, 2·30. Calc. for $Pt(en)(SCN)_2$: Pt, 52·5; C, 12·9; H, 2·16%).

This compound has the properties of the compound described by GROSSMANN and SCHÜCK. It is not soluble in water and melts with decomposition at 150–170°C. Analyses alone do not distinguish between $Pt(en)(SCN)_2$ and $[Pt(en_2][Pt(SCN_4]$. Therefore, these two compounds were prepared independently. The first was prepared by the reaction of $K_2Pt(SCN)_4$ with one equivalent of ethylenediamine and the second by the addition of $K_2Pt(SCN)_4$ to $[Pt(en)_2]Cl_2$. The colour of the compound in question and its infra-red spectrum are identical with $Pt(en)(SCN)_2$ and greatly different from $[Pt(en)_2][Pt(SCN)_4]$.

The infra-red spectra were determined in the rocksalt region on a Baird Associates instrument. A superimposed polystyrene spectrum served as calibration. Measurements were made on the solids using the KBr waffer and nujol mull techniques. Measurements were also made on dimethylsulphoxide and dimethylformamide solutions. Data on the SCN stretching vibration frequencies are given in Table 4.

The rate of hydrolysis of *trans*-$Pt(en)_2(SCN)_2^{2+}$ was determined by measuring the rate of release of CNS^- by the Volhard method. All of the reaction mixtures contained 0·005 M $[Pt(en)_2(SCN)_2](NO_3)_2$ and were kept thermostated in the dark. At a temperature of 25·0° both CNS^- ions are released in less than 10 min at pH 8 but there is essentially no CNS^- in a pH 1 solution even after 5 hr. The rapid release of CNS^- at pH 8 is a result of hydrolysis and not reduction to $Pt(en)_2^{2+}$. Data collected at 50·0° in 0·1 M $HClO_4$ gave a linear first-order plot for the release of the first CNS^- with a rate constant of $k_1 = 2{\cdot}1 \times 10^{-3}$ min^{-1}. The second CNS^- is hydrolysed at these conditions with a rate constant of $k_2 = 8 \times 10^{-4}$ min^{-1}.

$$Pt(en)_2(SCN)_2^{2+} \xrightarrow[k_1]{H_2O} Pt(en)_2(SCN)OH^{2+} \xrightarrow[k_2]{H_2O} Pt(en)_2(OH)_2^{2+} \qquad (7)$$

Addition of five mole per cent of $[Pt(en)_2](ClO_4)_2$ to the above reaction mixture does not markedly alter the rate of hydrolysis.

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TABLE 4.—INFRA-RED ABSORPTION IN THE SCN STRETCHING REGION FOR $[Pt(en)_2(SCN)_2](NO_3)_2$ AND SOME RELATED COMPOUNDS

Compound	KBr (cm^{-1})	Dimethylsulphoxide†		Dimethylformamide†	
		Freq. (cm^{-1})	Abs.§	Freq. (cm^{-1})	Abs.§
$[Pt(en)_2(SCN)_2](NO_3)_2$	2145, 2085 ‖	2050	162	2065	160
NaCNS	2065	2065	156	2065	148
$K_2Pt(SCN)_6$	2105	2115, 2055	—	2120	55
$K_2Pt(SCN)_4$	2105	2115, 2055	—	2120	175
$NH_4[Cr(NH_3)_2(NCS)_4]$	2120	2090	348	2090	370

† Dimethylsulphoxide solutions of $K_2Pt(SCN)_6$ and $K_2Pt(SCN)_4$ contained approximately 30 per cent of ionic CNS^-, as determined colorimetrically with Fe(III). The $[Pt(en)_2(SCN)_2](NO_3)$ solution contained 15% CNS^- and the $NH_4[Cr(NH_3)_2(NCS)_4]$ solution gave only a very faint test for CNS^-.

‡ Dimethylformamide solutions of $K_2Pt(SCN)_6$ and $K_2Pt(SCN)_4$ contained 3% CNS^- and the $[Pt(en)_2(SCN)_2](NO_3)_2$ solution contained 35% CNS^-. Only a very weak test for CNS^- was obtained with the solution of $NH_4[Cr(NH_3)_2(NCS)_4]$.

§ Molar absorptivity on the basis of moles of thiocyanate.

‖ 2130 and 2075 by Nujol–mull technique.

DISCUSSION

It has been shown that Pt(II)–Pt(IV) exchange in the system $Pt(1\text{–}pn)_2^{2+}$–*trans*-$Pt(en)_2Cl_2^{2+}$ is catalysed by different anions, X^-. Data in Table 1 indicate that Br^-, CNS^-, CN^-, Cl^-, CNO^- and NO_2^- are good catalysts whilst ClO_4^-, $C_2H_3O_2^-$, F^- and NO_3^- are poor with OH^- and SO_4^{2-} being intermediate. The bridged mechanism proposed to explain this catalysis, as outlined in equations (3) through (6), indicates that substitution reactions may occur in the systems with the better reagents but not those with the poor reagents. This has been amply substantiated by isolating substitution products of the type *trans*-$Pt(en)_2X_2^{2+}$ from reaction mixtures containing the more effective reagents. However, salts of the starting material, *trans*-$Pt(en)_2Cl_2^{2+}$ were isolated from similar reaction mixtures of the less reactive materials. The reaction with OH^- lead to appreciable reduction of Pt(IV).

That substitution reactions of *trans*-$Pt(en)_2Cl_2^{2+}$ seem to require catalytic amounts of Pt(II) was demonstrated for its reaction with HBr and with KCNS. For the former, it was observed that there is no replacement of Cl^- by Br^-, unless catalytic amounts of $Pt(en)_2^{2+}$ are added to the reaction mixture. However, *trans*-$Pt(en)_2Cl_2^{2+}$ does react with KCNS to yield $Pt(en)_2(SCN)_2^{2+}$, and a similar reaction occurs even if the solution of the dichloro complex is first treated with enough Ce(IV) to oxidize any catalytic amounts of Pt(II). This would indicate that Pt(II) catalysis is not required. However, the data in Table III show that the thiocyanate reaction is definitely catalysed by $Pt(en)_2^{2+}$. It also shows that Ce(IV) virtually stops the reaction at first but that it then proceeds autocatalytically. Thus, it appears that some *trans*-$Pt(en)_2Cl_2^{2+}$ is being reduced by CNS^-, particularly at the high concentrations used to prepare the dithiocyanato complex. Therefore, the catalyst is being generated by reduction of the starting material.

The synthesis of $Pt(en)_2(SCN)_2^{2+}$ salts is described here for what is believed to be the first time. GROSSMANN and SCHÜCK had reported the preparation of a very

insoluble material, which they formulated as $[Pt(en)_2(SCN)_2](CNS)_2$, by the reaction of $K_2Pt(SCN)_6$ with two equivalents of ethylenediamine. In our hands this reaction also gave an insoluble product but it was found to be the platinum(II) compound $Pt(en)(SCN)_2$. This result is analogous to the observation of CLEVE[7] that the reaction between $K_2Pt(SCN)_6$ and $(NH_4)_2CO_3$ yields $Pt(NH_3)_2(SCN)_2$.

The structure of the complex $Pt(en)_2(SCN)_2^{2+}$ is not known. Proof of structure will have to await X-ray analysis. However, there is some evidence that the complex is the *trans* isomer and that both thiocyanates are bound to platinum through the sulphur, Pt–SCN.

Tentative assignment of the *trans* structure is made on the basis of the following observations. First the infra-red spectrum of the complex in the N—H and C—H regions is the same as that for *trans*-$Pt(en)_2Cl_2^{2+}$. If $Pt(en)_2(SCN)_2^{2+}$ were the *cis* isomer, it would be expected to show some splitting, of these absorption bands.[8] Second the complex is readily reduced to $Pt(en)_2^{2+}$, a property shown by the Russian chemists to be characteristic of the *trans* isomers of diacidotetrammine-platinum(II) complexes.[1] Finally, the reaction of $Pt(en)_2(SCN)_2^{2+}$ with HCl and HBr yields *trans*-$Pt(en)_2Cl_2^{2+}$ and *trans*-$Pt(en)_2Br_2^{2+}$ respectively.

An attempt was made to determine whether platinum is bound to the sulphur or to the nitrogen of the co-ordinated thiocyanate. This was done by comparing the infra-red spectrum of this complex in the SCN stretching region with that of compounds of known structure. The results obtained are shown in Table 4. These data show that the absorption bands are at almost the same frequency for $Cr(NH_3)_2(NCS)_4^-$, where the linkage is Cr—NCS[9] and $Pt(SCN)_{4\text{ or }6}^{2-}$, where the linkage is Pt—SCN.[10] However, in dimethylformamide solution the molar absorptivity of the former is greater than that for $Pt(SCN)_{4\text{ or }6}^{-2}$. The same low molar absorptivity was observed for $Pt(en)_2(SCN)_2^{2+}$ and on this basis it is tentatively assigned a Pt—SCN linkage. That the SCN stretching vibration frequency of $Pt(en)_2(SCN)_2^{2+}$ is similar to that of NaCNS and different from that of the other metal complexes tested either M—NCS or M—SCN, is not understood. This cannot be the result of solvation to yield thiocyanate ion in solution. Colorimetric determinations with iron (III) show that these solutions contain only a small amount of ionic thiocyanate.

It is of interest to note that the bridged mechanism for substitution may lead to the formation of a complex containing two types of thiocyanate, viz. Pt—SCN and Pt—NCS,

$$\begin{array}{l} \begin{matrix} en \\ Cl—Pt—SCN^{2+} \\ en \end{matrix} + \begin{matrix} en \\ Pt—SCN^{+} \\ en \end{matrix} \rightleftharpoons \begin{matrix} en & en \\ Cl—Pt—SCN—Pt—SCN^{3+} \\ en & en \end{matrix} \rightleftharpoons \\ \qquad\qquad \begin{matrix} en & en \\ Cl—Pt^{+} + SCN—Pt—SCN^{3+} \\ en & en \end{matrix} \end{array} \qquad (8)$$

No linkage isomers of thiocyanate complexes have yet been reported, and there is no

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[9] Y. SAITO, Y. TAKEUCHI and R. PEPINSKY, *Z. Krist.* **106**, 476 (1955); *Bull. Chem. Soc. Japan* **29**, [4] 319 (1957).
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evidence for two types of thiocyanate in $Pt(en)_2(SCN)_2^{2+}$. This may result from further reaction of the original product to yield the more stable isomer

$$\begin{array}{l} \text{en} \\ \text{NCS—Pt}^{+} \\ \text{en} \end{array} + \begin{array}{l} \text{en} \\ \text{SCN—Pt—SCN}^{2+} \\ \text{en} \end{array} \rightleftharpoons \begin{array}{l} \text{en} \quad \text{en} \\ \text{NCS—Pt—SCN—Pt—SCN}^{2+} \\ \text{en} \quad \text{en} \end{array} \rightleftharpoons$$

$$\begin{array}{l} \text{en} \quad \text{en} \\ \text{NCS—Pt—SCN}^{2+} + \text{Pt—SCN}^{+} \\ \text{en} \quad \text{en} \end{array} \qquad (9)$$

A similar observation was made by EDWARDS and CARLIN[11] in their attempt to prepare $(H_2O)_5Cr—SCN^{2+}$.

The rate of acid hydrolysis of *trans*-$Pt(en)_2(SCN)^2{}_2^+$ at 50° in the dark is appreciable ($k_1 = 2{\cdot}1 \times 10^{-2}$ min^{-1}) whereas under similar conditions *trans*-$Pt(en)_2Cl_2^{2+}$ shows no sign of hydrolysis even after standing several days. This is surprising because chloro complexes of Co(III) and Cr(III) react much more rapidly than do analogous thiocyanato complexes.[12] However, it should be remembered that the bonding in Co(III) and Cr(III) is M—NCS whereas that in Pt(IV) is perhaps Pt—SCN. In contrast to this, recent studies[13] have shown that thiocyanato complexes of Pt(II) do react more slowly than do corresponding chloro compounds. In these Pt(II) compounds the Pt—SCN bond strength is perhaps enhanced due to π-bonding. It is of interest to note that the rapid hydrolysis of *trans*-$Pt(en)_2(SCN)_2^{2+}$ is in agreement with its infra-red spectrum which suggests a relatively weak Pt—SCN bond.

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SOME INVESTIGATIONS ON THE URANIUM : THORIUM : CARBON SYSTEM

N. BRETT, D. LAW and D. T. LIVEY
Atomic Energy Research Establishment, Harwell, Didcot, Berks

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Abstract—The dicarbides of uranium and thorium have been prepared by sintering mixtures of the elemental powders at 1500°C and 1800°C respectively. Uranium dicarbide is stable in air at room temperature; in pellet form as prepared it breaks down in dry air between 200° and 300°C and in moist argon between 300° and 400°C. Thorium dicarbide decomposes rapidly at room temperature by reaction with atmospheric moisture.

The system UC_2–ThC_2 has been investigated by preparation of fused specimens of mixed crystals and examination of these by X-ray and by microscope. The evidence from both sources shows that the system is one of complete solid solubility although the middle ranges of composition are poorly crystalline.

Stability tests on mixed crystals of dicarbides show that they are stable to between 200° and 400°C in dry oxygen, the temperature of oxidation increasing from ~200°C at the ThC_2 end of the system to ~400°C at the UC_2 end. Oxidation forms mixed crystals of UO_2–ThO_2 cubic solid solution.

Some information is given on uranium–thorium–carbon compacts containing principally the monocarbides. X-ray examination indicates that this system also is one of complete solid solubility.

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URANIUM and thorium form several refractory carbides which are of particular interest at the present time because of their potential application, as fuel and breeder materials respectively, in nuclear reactors. Emphasis is now being placed in raising operating temperatures in gas-cooled reactors for improved efficiency and the high-temperature fuels necessary to achieve this may be of the oxide type or carbide type. Currently, oxide materials are undergoing intensive technological investigation for use as solid fuels, and while the general technology of carbides is somewhat less developed than that of the oxides, for general fuel performance, they may have the advantage of higher thermal conductivity and greater strength; against this may be placed poorer corrosion resistance and greater difficulties in fabrication. Nevertheless, there is a need for extensive development of these carbide materials as future fuels, because of their promising properties.

The general properties of uranium and thorium carbides are shown in Table 1. Three methods have been reported for the preparation of uranium dicarbide;

(a) fusion of mixed uranium–graphite compacts;[5]
(b) reaction of the elements at 2400°C;[6,7]
(c) reduction of the oxide either UO_2 or U_3O_8 above 2000°C.[6,7]

[1] H. A. WILHELM, P. CHIOTTI, A. L. SNOW and A. M. DAANE, *J. Chem. Soc.* Supplement No. 2, 318 (1949).
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TABLE 1.—GENERAL PROPERTIES OF THE CARBIDES OF URANIUM AND THORIUM

Carbon (w/o)	Density (gm/cc)	Melting point (°C)	Structure
ThC 4·92	10·67	2625	f.c.c. $a = 5{\cdot}34$ A°[1]
ThC_2 9·38	9·6	2655	$a = 6{\cdot}53$ A° $B = 104°$ $Z = 4$ mono-clinic $b = 4{\cdot}24$ A°[2] $c = 6{\cdot}56$ A° (Figs. 1 and 2)
UC 4·90	13·6	2450–2500	f.c.c. $a = 4{\cdot}95$ A°[1,3]
U_2C_3 7·0	12·9	Decomposes 1800	b.c.c. $a = 8{\cdot}088$ A°[4]
UC_2 9·16	11·7	2350–2400	b.c. tetragonal CaC_2 type structure $a = 3{\cdot}52$ A°[3] (Figs. 3 and 4) $b = 5{\cdot}99$ A°

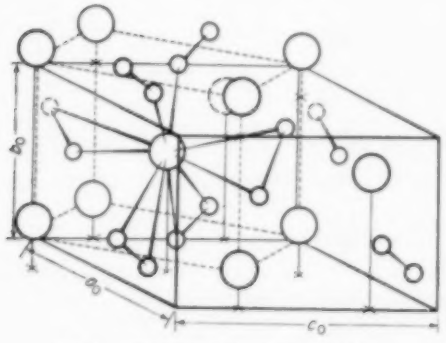

FIG. 1.—Structure of thorium dicarbide.

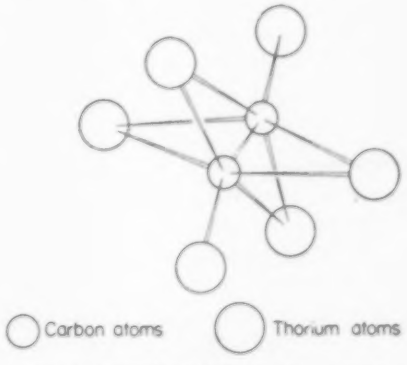

FIG. 2.—Grouping of thorium-atoms about the C–C bond in ThC_2.

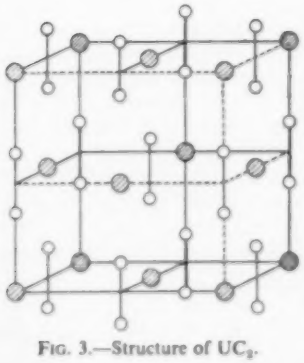

FIG. 3.—Structure of UC_2.

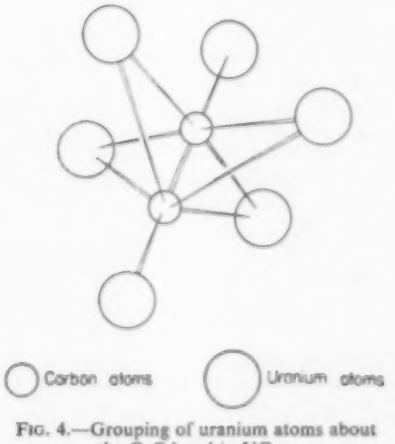

FIG. 4.—Grouping of uranium atoms about the C–C bond in UC_2.

Observations on the stability of uranium dicarbide have also been reported. MURRAY *et al.*[8] and SPEDDING[9] found that uranium dicarbide compacts decomposed on exposure in a moist atmosphere. SPEDDING also reported that no oxidation occurred in an air stream at 300°C but complete oxidation within 4 hr between 400–500°C. LITZ[7], who investigated the hydrolysis of uranium dicarbide both in water and water vapour, found that liquid hydrolysis gave erratic results due to the formation of clumps of dicarbide and suggested that the dicarbide was protected by an envelope of gaseous hydrolysis products. Under an atmosphere of superheated steam

TABLE 2.—DATA ON URANIUM, THORIUM AND GRAPHITE POWDERS

Powder	Preparation	Particle size (μ)
Uranium	Reduction of UO_3 by calcium	Mean 8
Thorium	Reduction of ThO_2 by calcium	95% < 40
UO_2	Reduction of U_3O_8 by hydrogen at 700°C	Mean 40
Graphite	Achesons graphite ground 24 hr in a rubber lined ball mill.	Mean 40

at low pressures, decomposition at 100°C gave mainly hydrogen (47 per cent), higher paraffins and methane (30 per cent); the hydrogen content increased with temperature to give 96 per cent hydrogen at 249°C.

Much less information is available on thorium dicarbide. TROOST[10] has prepared it in the electric arc furnace and WILHELM and CHIOTTI[11] by sintering compacts of thorium and carbon at 2400°C and by melting thorium in graphite crucibles at 2700°C.

Apart from its rapid hydrolysis in moist air, nothing has been reported on the general stability of thorium dicarbide.

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1. APPARATUS AND PROCEDURE

Preparation of dicarbides

In these studies three methods of preparation were used employing uranium and thorium metal powders and fine graphite powder. The properties of the powders used are shown in Table 2.

Sintering. The metal and graphite powders were intimately mixed in a glass bottle and cold pressed at 20 tons/in² in a tungsten carbide die. The compacts were then sintered in a purified argon atmosphere in a rhodium-wound furnace capable of operating at 1800°C. Sintering temperatures were measured by an 80 Pt-20 Rh/60 Pt-40 Rh thermocouple. The furnace tube was attached to a glove box with an argon atmosphere so that the specimens could be withdrawn into the box when cool. Thorium dicarbide decomposed unless stored under an inert liquid for which purpose paraffin was found suitable.

Hot pressing. Compacts of stoicheiometric mixtures of powders were hot pressed at 1700°C in graphite dies in a carbon tube resistance furnace under 1 ton/in². Temperature measurement was made with an optical pyrometer previously calibrated against a Pt/Rh thermocouple.

Fusion. Compacts of the appropriate powders previously hot pressed at 1700°C (to preform the

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dicarbides and to provide cohesion) were fused under an argon arc. To avoid pick up of oxygen a zirconium getter was heated simultaneously with the specimen. From the molten condition the specimens cooled very rapidly to a dull red heat, effectively quenching them. The specimens were then annealed at 1800°C under argon in a recrystallized alumina boat. After several runs the boat discoloured slightly but in general there was no reaction. Above 1800°C a graphite tube furnace was used, the specimen being supported at its edges in a graphite crucible. Samples for microscopic and X-ray examination were obtained by the fusion technique.

Preparation of microspecimens

Specimens were prepared for metallographic examination by mounting in diakon, rough polishing under paraffin on papers and finally polishing on a terylene cloth impregnated with 1-3 μ diamond dust suspended in vaseline. Those alloys rich in uranium (>70 w/o UC_2) were etched in a solution containing equal parts of water, nitric acid and acetic acid; those rich in thorium (<70% UC_2) etched sufficiently on exposure to atmosphere.

X-Ray technique

The Debye-Scherrer powder method was employed, using a Phillips 11·46 cm diameter camera, the Straumanis method of film mounting and copper K_α radiation. Samples of powder were prepared by grinding the carbides under paraffin to minimize oxidation by hydrolysis. The wet, ground powder was then introduced into a glass capillary tube filled with paraffin and the ends sealed to give a specimen 0·5 mm diameter and 2 cm long. To facilitate the interpretation of complex patterns, standard patterns were obtained for uranium and thorium dicarbides from samples prepared by fusion of stoicheiometric mixtures of the elements. These patterns were confirmed by comparison with the A.S.T.M. powder data cards for uranium and thorium dicarbides.

Stability tests

These consisted either of exposure of the massive or powdered samples to the atmosphere or of heating them in atmospheres of moisture, air or oxygen.

2. RESULTS

Preparation of dicarbides

Uranium dicarbide. Sintered compacts of 70/30 w/o uranium–graphite powders held for 1 hr at 1000°C, followed by one hour at 1400°C, showed, on X-ray analysis, uranium dicarbide, graphite and a trace of uranium monocarbide; by raising the final sintering temperature to 1500°C the monocarbide was eliminated. Specimens of uranium dicarbide for stability tests were prepared by this method.

Compacts of UO_2/graphite, 80/20 w/o, sintered for 1 hr at 1800°C analysed approximately 70/30 w/o UC_2/UC. By using 70/30 w/o UO_2/graphite mixtures as starting material, i.e. 10 w/o graphite in excess of that required for stoicheiometric UC_2, the monocarbide was eliminated. Similar compacts sintered in a carbon-tube furnace operating on unpurified argon always showed UO_2 to be present in the final sample. This is probably because the uranium dicarbide is re-oxidized on cooling due to a reversal of the carburizing reaction $UO_2 + 4C \rightleftharpoons UC_2 + 2CO$. The partial pressure of oxygen in unpurified argon is $\sim 2 \times 10^{-3}$ atm; hence $p_{CO} \simeq 2 \times 10^{-3}$ atm in the carbon tube furnace, and as this value is less than the equilibrium partial pressure of CO for the above reaction at 1800°K (0·11 atm) and greater than the equilibrium pressure at 1000°K (7×10^{-12} atm) oxidation will occur on cooling.

Thorium dicarbide. Attempts to prepare thorium dicarbide at 1500°C in argon as described for uranium dicarbide were not successful and thoria always resulted. At 1700°C a trace of thorium dicarbide was detected; it is believed that the dicarbide is formed but not retained as even a trace of moisture rapidly causes disintegration of the dicarbide compacts. It was finally prepared from an 85/15 w/o thorium–graphite

mixture sintered at 1800°C in argon, the compacts being quickly transferred to paraffin when cool. The argon was passed over uranium turnings at 600°C and through calcium chloride and magnesium perchlorate driers to remove traces of oxygen and moisture.

Mixed dicarbides of thorium and uranium. These were prepared by pressing stoicheiometric amounts of uranium, thorium and graphite powders in graphite dies at 1700°C and 1 ton/in², followed by fusion of the compact in an argon arc furnace. Specimens were then stored under paraffin until examination. Chemical analyses of a series of specimens prepared in this way are shown in Table 3.

TABLE 3.—'PREPARED' AND ANALYSED COMPOSITIONS OF UC_2/ThC_2 COMPACTS

UC_2/ThC_2	Prepared		Analysed	
	Uranium metal in total metal (w/o)	C (w/o)	Uranium in total metal (w/o)	C (±1%) (w/o)
10/90	10	9·35	12·0	4·75
30/70	30	9·31	34·2	11·1
50/50	50	9·27	47·8	9·4
55/45	55	9·26	56·0	10·1
60/40	60	9·25	58·0	12·0
70/30	70	9·22	67·0	10·4
80/20	80	9·20	80·0	13·8
90/10	90	9·19	91·9	10·2

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Taking into account the smallness of the total sample (2 cc), the fact that the material has been hot pressed, fused and approximately 1 g taken for chemical analysis, the agreement between prepared and analysed uranium and thorium contents is considered satisfactory. Except in one instance the carbon contents are high. This is probably due to carbon pick up during hot pressing and is not a disadvantage since it ensures that sufficient carbon is present for complete dicarbide formation. The one low analysed carbon content is not in agreement with either X-ray analysis or microscopic evidence (shown later).

Samples of uranium dicarbide, thorium dicarbide and mixed dicarbides for metallographic and X-ray examination were prepared by this method. An initial series of preparations, however, showed incomplete formation of the dicarbides and the samples contained both monocarbides and dicarbides of uranium and thorium. The information from these is discussed in Section 3.

X-ray and metallographic examination

The results of X-ray and metallographic examination are summarized in Table 4 and photomicrographs are shown in Figs. 5–7.

The lines on the X-ray patterns of all compositions between the end members of the UC_2–ThC_2 join had weak intensities and decreasing crystallinity towards the centre compositions was noted. However, the trend of the changes taking place is

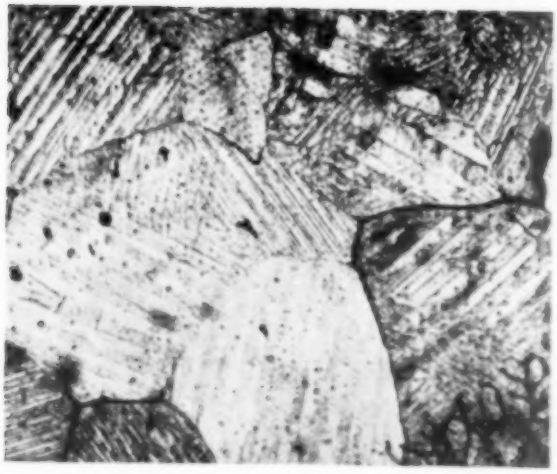

FIG. 5.—Microstructure of ThC_2 as fused.

FIG. 6.—Microstructure of 30 UC_2/70 TnC_2, annealed at 1900°C.

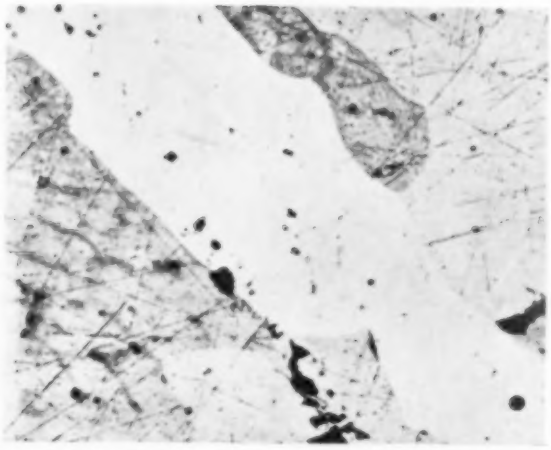

FIG. 7.—Microstructure of UC_2 as fused.

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TABLE 4.—RESULTS OF X-RAY AND METALLOGRAPHIC EXAMINATION OF UC_2/ThC_2 COMPACTS

Composition (as prepared) (wt %)	X-ray results	Microstructure observations
ThC_2	Diffraction pattern verified as ThC_2 by comparison with A.S.T.M. powder data.	Typical ThC_2 appearance[11] Fig. 5.
10 UC_2/90 ThC_2	Mainly ThC_2 type; cell size less than standard pattern; graphite also present.	ThC_2 appearance with large grains showing banded structure. The sample after annealing at 1900°C was unchanged from the fused structure.
30 UC_2/70 ThC_2	Mainly ThC_2 type; cell size less than previous sample; less crystalline structure.	Similar appearance to the 10 UC_2/90 ThC_2 sample. Fig. 6 shows the appearance after annealing at 1900°C.
50 UC_2/50 ThC_2	ThC_2 type; Cell size appreciably smaller than the 30 UC_2/70 ThC_2 sample; poorly crystalline.	Banded structure still evident but the surface contained many cracks and fissures.
55 UC_2/45 ThC_2	Very diffuse pattern of ThC_2 type. Poor crystallinity and showing considerable distortion from the end structure.	Similar in appearance to 50 UC_2/50 ThC_2.
60 UC_2/40 ThC_2	Distorted structure resembling UC_2 type; diffuse lines, poorly crystalline.	Mainly a single phase with some banded grains. Small amounts of a second phase which rapidly air etches.
70 UC_2/30 ThC_2	UC_2 type; diffuse lines.	Predominantly UC_2 appearance. Fused and annealed micrographs were similar.
80 UC_2/20 ThC_2	UC_2 type; cell size larger than that given by the standard pattern.	Gave poor micrograph due to heavily cracked surface.
90 UC_2/10 ThC_2	UC_2 type; cell size intermediate to the 80 UC_2/20 ThC_2 and the UC_2 standard sample.	Typical single-phase UC_2 appearance.
UC_2	UC_2. Diffraction pattern verified by comparison with A.S.T.M. data.	Typical of UC_2 structure. Fig. 7 shows the fused appearance after etching.

quite clear. The evidence shows that, at either end of the UC_2/ThC_2 join, the structure is single phase and is that of the predominating carbide with a change in cell size. At the composition 50 UC_2/50 ThC_2, which is the most probable for the maximum distortion of the terminal structures, the X-ray pattern is a very diffuse one of the ThC_2 type showing a poorly crystalline structure. Increase in uranium content to 55 UC_2/45 ThC_2 again shows a very diffuse pattern of the ThC_2 type, while a further increase to 60 UC_2/40 ThC_2 shows a poorly crystalline structure which resembles a distorted UC_2 type. A single phase was shown throughout under the microscope, the banded structure being typical of ThC_2 and may be due to a phase transformation at high temperature or to a slight precipitation of monocarbide along certain crystallographic planes. The centre compositions were later examined more closely. Compacts were hot pressed, fused and annealed as before. Micrographs showed single phase compositions in each case with some evidence of a banded structure. X-Ray patterns showed a poorly crystalline structure of the UC_2 type.

Complete solid solubility therefore exists between the two dicarbides with pronounced distortion of the crystalline structures increasing towards the centre compositions; no evidence was obtained which indicated a breakdown to more than one phase at these compositions.

Although the structures of uranium dicarbide and thorium dicarbide are differently described (body centred tetragonal and *C*-centred monoclinic respectively) the complete solid solubility is feasible because the groupings of uranium and thorium atoms about their respective carbon bonds are similar. The structures are shown in Figs. 1–4. In uranium dicarbide, the C—C bonds alternate with uranium atoms to form straight line chains, and four uranium atoms are grouped in a plane normal to the C—C bond, which intersects the bond midway between the carbon atoms. In thorium dicarbide, the C—C bonds and thorium atoms form a chain which is not straight; otherwise, the grouping is the same.

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Stability tests

Uranium dicarbide. In Table 5 the results of a number of simple stability tests on uranium dicarbide and graphite pellets are shown. In runs (1) and (2) the pellets used were prepared at 1400°C and contained a trace of monocarbide. These tests show that uranium dicarbide as prepared does not decompose by reaction with water-vapour at room temperature. It is stable in air up to 200°C but by 300°C has decomposed to form U_3O_8. In argon saturated with water-vapour, decomposition does not take place until above 300°C when UO_2 is formed in contrast to the formation of U_3O_8 as in air.

Thorium dicarbide. Thorium dicarbide either in massive or powder form decomposed rapidly to thoria in the presence of moisture.

Mixed dicarbides of thorium and uranium. On exposure to the normal atmosphere, compositions from ThC_2 to 50 UC_2/50 ThC_2 decomposed within 12 hr to the oxides. The compositions 60 UC_2/40 ThC_2 and 70 UC_2/30 ThC_2 finally decomposed after three days in air while the 80 UC_2/20 ThC_2 and 90 UC_2/10 ThC_2 compacts showed no sign of breakdown after a week.

Specimens were also heated in dry oxygen and some of them examined by X-ray analysis after treatment. The results are summarized in Table 6.

From Table 6, compacts rich in thorium dicarbide are stable in dry oxygen up to 200°C, oxidation starting between 200–300°C. That this was not simply an effect due

to the large particle size was shown when one sample, of composition 10 UC_2/90 ThC_2, was powdered under acetone, dried in the furnace under a stream of oxygen, raised to 200°C and held for 12 hr at that temperature. X-Ray analysis showed that no oxidation has occurred.

As the uranium dicarbide content is increased, the temperature of oxidation rises, being some 200°C higher at the composition 80 UC_2/20 ThC_2. The X-ray patterns

TABLE 5.—RESULTS OF STABILITY TESTS ON URANIUM DICARBIDE AND GRAPHITE PELLETS

Treatment of UC_2 + C pellet	X-Ray analysis result
1. Pellet uncrushed aged 1 day in air	UC_2 + C + trace UC
2. Pellet crushed aged 3 days in air	UC_2 + C + trace UC
3. Pellet ground periodically in an agate mortar with water for a period of a week.	UC + C
4. Pellet stored several weeks in argon, ground and heated to 200°C for 30 min in air.	UC_2 + C + UC
5. As above, temperature raised to 300°C.	U_3O_8 + C Heavy background
6. As above, temperature raised to 400°C.	U_3O_8 + C
7. Heated in a stream of argon containing the saturation vapour pressure of water at 20°C for 1 hr at:	
(a) 100°C	UC_2 + C
(b) 200°C	UC_2 + C
(c) 300°C	UC_2 + C + trace of UO_2
(d) repeat 300°C	UC_2 + C
(e) 400°C	UO_2 + C
(f) 500°C	UO_2 + C

for the oxides formed from the samples 60 UC_2/40 ThC_2 and 80 UC_2/20 ThC_2 corresponded to the cubic solid solution of ThO_2 in UO_2, no free ThO_2 being detected. Pure UO_2 would form U_3O_8 under these conditions[12] so that the presence of ThO_2 has stabilized the cubic structure. This is similar to the effect observed by ANDERSON *et al.*[13] who found stabilization in air up to 1400°C of the cubic mixed crystals of oxide UO_2/ThO_2 for UO_2 contents less than 78%.

X-Ray and metallographic data on specimens containing both monocarbides and dicarbides

These results were obtained because the first attempts to fabricate the dicarbides resulted in specimens consisting mainly of monocarbides. The method consisted of hot pressing at 600°C followed by fusion. Results of metallographic and X-ray examination are shown in Table 7.

[12] P. MURRAY, and D. T. LIVEY, *Progress in Nuclear Energy* Series V, Vol. 1, p. 448. Pergamon Press, London (1959).
[13] J. S. ANDERSON, D. N. EDGINGTON, L. E. J. ROBERTS and E. WAIT, *J. Chem. Soc.* 3324 (1954).

TABLE 6.—OBSERVATIONS ON OXIDATION TEMPERATURES OF THORIUM/URANIUM DICARBIDE COMPACTS

Composition of compact as prepared	Treatment	Observations visual and X-ray
ThC_2	Held at 300°C for 24 hr	Thin coating of oxide formed
	Temperature raised to 500°C	Fully oxidised to thoria
10 UC_2/90 ThC_2	Held at 20°C for 24 hr	No change in appearance of compact
	Temperature raised to 75°C and held 72 hr	No change
	Temperature raised to 150°CO and held 24 hr	No change
	Temperature raised to 200°C and held 24 hr	Bright metallic blue surface appearance but compact otherwise stable
	Temperature raised to 300°C and held 24 hr	Surface coating of oxide formed
30 UC_2/70 ThC_2	Treated as previous sample	Similar to 10 UC/90 ThC_2 sample. After heating at 300°C X-ray analysis showed ThC_2 type structure + ThO_2
50 UC_2/50 ThC_2	Treated as the 10 UC_2/90 ThC_2	Metallic blue surface appearance
	Held a further 24 hr at 300°C	A veneer of oxide formed which X-ray analysis showed to be a ThO_2 type pattern + ThC_2 type pattern
60 UC_2/40 ThC_2	Held at 300°C for 24 hr	Blue surface appearance
	Raised to 400°C for 24 hr	Compact fragmented but did not appear oxidized
	Raised to 500°C for 24 hr	Gave UO_2 type pattern + a trace of U_3O_8
70 UC_2/30 ThC_2	Held at 300°C for 24 hr then for a further 24 hr	Blue surface appearance Compact had fragmented
	Raised to 400°C for 24 hr	X-ray analysis showed a UC_2 type, structure with a larger cell size than UC_2; i.e. unchanged
	Raised to 500°C for 24 hr	Sample oxidized and formed powder
80 UC_2/20 ThC_2	Treated as the 70 UC_2/30 ThC_2 sample	Both formed UO_2 type compounds 500°C

Although these samples are complicated by the presence of both mono and dicarbides, several points emerge.

1. The predominant structure in most cases was that of the monocarbide, with a lattice parameter intermediate to that of the end members uranium monocarbide and thorium monocarbide. The change in lattice parameter seemed to be progressive throughout the series and indicates complete solid solubility of the monocarbides. This would be expected from the similarity in their structures (cubic NaCl type).

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TABLE 7.—RESULTS OF X-RAY AND METALLOGRAPHIC EXAMINATION OF MIXED MONO AND DICARBIDES OF URANIUM AND THORIUM

Composition (as prepared)	X-ray results	Microstructure observations
10 UC_2/90 ThC_2	ThC_2 + ThC type pattern; lattice parameter of the ThC smaller than standard; cell size of the ThC_2 unchanged	As fused structure showed well defined grains of ThC_2 with ThC tending to precipitate. Annealing at 2000°C produced a Widdermanstatten structure, with precipitation of ThC.
30 UO_2/70 ThC_2	ThC_2 + ThC type pattern; ThC has smaller L.P.: than the 30 UC_2/70 ThC_2 sample	Complete precipitation of the monocarbide takes place on annealing
60 UC_2/40 ThC_2	UC type structure; L.P. much larger than pure UC; UC_2 also present but diffuse diffraction pattern	
70 UC_2/30 ThC_2	UC type pattern; smaller L.P. than the 60 UC_2/40 ThC_2 sample and larger than pure UC	
80 UC_2/20 ThC_2	UC_2 + UC type pattern; L.P. of UC structure smaller than previous sample and larger than pure UC	
90 UC_2/10 ThC_2	UC_2 + UC type; L.P. of UC structure intermediate to the 80 UC_2/20 ThC_2 type and pure UC lattice parameters	

2. In those samples where dicarbide was detected by X-rays, the lattice parameter was unchanged from that of the pure compound, so that the alloying member seems to remain preferentially in solid solution in the monocarbide.
3. The dicarbide structure appears to be able to hold a considerable quantity of monocarbide in solid solution since specimens annealed at 2000°C show precipitation of monocarbide. This agrees with WILHELM and CHIOTTI[11] who found that ThC_2 and ThC enter into solid solution above 2200°C and precipitate from one another below this temperature.

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THE SYSTEM AgF–HF–H_2O AT 0° AND −15°

H. J. THOMAS and A. W. JACHE
Chemistry Department, Agricultural and Mechanical College of Texas,
College Station, Texas

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Abstract—The system AgF·HF_2O has been investigated at 0° and −15°. The solid phases at 0° are AgF, AgF·$2H_2O$, AgF·$4H_2O$, 3AgF·2HF, AgF·2HF, AgF·3HF, AgF·5HF, and 6AgF·7HF·$2H_2O$. At −15° they are AgF, AgF·$2H_2O$, AgF·$4H_2O$, AgF·HF, AgF·3HF and AgF·5HF.

LITTLE work has been done on ternary systems involving silver fluoride. TANNANAEV and NEKHAMKINA[1] have studied the system silver fluoride, aluminium fluoride and water. TALIPOV *et al.*[2] have investigated the system silver fluoride, magnesium fluoride and water. GUNTZ and GUNTZ[3] have investigated parts of the system silver fluoride–hydrogen fluoride–water (AgF–HF–H_2O) using only aqueous hydrofluoric acid. Their results are hard to interpret and the abstractors have apparently overlooked this phase of their work. They reported the solid phases at 0° are AgF·2HF, AgF, AgF·$2H_2O$. AgF·$4H_2O$ and 3AgF·$5H_2O$. The need for a complete study of this system appeared to be indicated.

We have studied this system at 0 and −15°, using Schreinemaker's wet residue method.[4]

EXPERIMENTAL

Samples were made up from distilled water, reagent grade aqueous HF and AgF prepared by the method of ANDERSON *et al.*[5] Some AgF (Harshaw specification 101) was also used. When HF of concentration greater than 48 per cent was needed, it was made up from mixtures of anhydrous HF and aqueous HF. The anhydrous HF used was the middle fraction obtained from a commercial cylinder. This was distilled from the cylinder into a polyethylene collection bottle and redistilled through an all polyethylene system. The first and last fractions of each distillation were discarded. The liquid HF could be saturated with AgF to reduce the vapour pressure and stored until needed.

Various mixtures of HF, H_2O and AgF were placed in 50 ml wide mouth polyethylene bottles. These were placed in an ethylene glycol–water bath whose temperature was regulated to ±0·06°. Agitation of the samples was achieved by attaching them to a rotating wheel mounted vertically in the bath. If no solid phase remained, more AgF was added, and the samples were returned to the wheel. After about three days liquid samples were taken and analysed. Agitation was stopped about four hours before the samples were taken. Liquid samples were taken by inserting a piece of tapered polyethylene tubing fitted to a polyethylene bottle which had been squeezed. The reduced pressure in the bottle caused the sample to be drawn up. A piece of polyethylene tubing sealed at one end was slipped over the end of the tapered tubing to prevent loss of HF during weighing. Parts of this liquid were discharged into 300 ml wide mouth polyethylene bottles containing ice and about 25 ml of water. Weights of these samples were determined by weighing the sample and contents before and after

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[2] SH. T. TALIPOV, D. A. ABDULLAEV and M. V. KIRSAHOVA, *Trudy Sredneaziat. Univ.* No. 40, *Khim. Nauk.* No. 5, 43–46 (1953); *Chem. Abstr.* **49**, 6712 (1955).
[3] A. GUNTZ and A. A. GUNTZ, JR., *Ann. Chim.* **2**, 101 (1915).
[4] F. F. PURDON and V. W. SLATER, *Aqueous Solution and the Phase Diagram.* Arnold, London (1946).
[5] F. A. ANDERSON, B. BAK and A. HILLEBERT, *Acta Chem. Scand.* **7**, 236 (1953); *Chem. Abstr.* **47**, 8569 (1953).

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TABLE 1.—ANALYSIS OF THE SOLUTIONS AND WET RESIDUES AT 0°C

Solutions (weight %)		Wet residues (weight %)		Composition of solid phase
HF	AgF	HF	AgF	
0·17	51·05	0·11	60·56	$AgF·4H_2O$
1·75	49·54	0·59	59·00	$AgF·4H_2O$
2·71	49·17	1·30	56·84	$AgF·4H_2O$
3·32	50·69	1·66	57·36	$AgF·4H_2O$
4·40	54·12	2·57	60·57	$AgF·4H_2O$
4·45	52·08	2·31	58·19	$AgF·4H_2O$
4·59	54·07	2·98	57·67	$AgF·4H_2O$ and $AgF·2H_2O$
5·71	60·86	1·79	73·50	$AgF·2H_2O$
7·46	62·13	3·87	57·36	$AgF·2H_2O$
9·92	64·21	7·79	72·35	AgF
12·70	65·88	7·67	79·07	AgF
14·66	63·27	13·31	68·35	3AgF·2HF
16·20	62·21	12·98	79·17	3AgF·2HF
17·84	60·27	13·90	75·91	3AgF·2HF
20·34	58·95	15·81	76·62	$6AgF·7HF·2H_2O$
23·57	55·80	17·73	73·20	$6AgF·7HF·2H_2O$
25·30	53·00	22·50	62·54	$6AgF·7HF·2H_2O$
29·51	50·20	24·98	59·99	$6AgF·7HF·2H_2O$
32·82	48·71	19·61	72·81	$6AgF·7HF·2H_2O$
34·06	47·43	16·95	77·71	$6AgF·7HF·2H_2O$
37·47	46·28	18·88	75·83	$6AgF·7HF·2H_2O$
38·64	45·72	21·55	71·54	$6AgF·7HF·2H_2O$
42·10	45·47	17·96	78·04	$6AgF·7HF·2H_2O$
40·76	47·84	28·50	68·51	AgF·2HF
42·17	47·37	28·99	68·03	AgF·2HF
47·51	42·82	35·25	60·04	AgF·2HF
50·22	39·36	36·82	60·16	AgF·3HF
55·38	38·56	41·21	56·61	AgF·3HF
56·46	39·57	43·26	56·37	AgF·5HF
Liquid HF[8]	38·20	—	—	—

discharge of samples. Samples were usually taken at daily intervals and equilibrium was assumed when successive analyses for HF and AgF gave consistent results.

Samples for analysis were treated with an excess of 1 N NaCl. The solutions were then titrated with 1 N NaOH solution using phenolphthalein as indicator. When the solution turned pink, a rubber policeman was used to break up the coagulated silver chloride to release occluded HF. The titration was continued until an end point was reached.

The AgCl from the samples were collected in fritted glass crucibles, washed with 0·01 N HNO_3 and water and weighed as AgCl.

DISCUSSION AND RESULTS

The results of the analyses of the solutions and wet residues are given in Tables 1 and 2 and representative points have been plotted in Figs. 1 and 2.

The solid phases existing at 0° are AgF, $AF·2H_2O$, $AgF·4H_2O$, 3AgF·2HF, AgF·2HF, AgF·3HF, $6AgF·7HF·2H_2O$ and presumably AgF·5HF. The HF(wt. per

[8] A. W. JACHE and G. H. CADY, *J. Phys. Chem.* **56**, 1106 (1952).

TABLE 2.—ANALYSIS OF THE SOLUTIONS AND WET RESIDUES AT −15°C

Solutions (weight %)		Wet residues, (weight %)		Composition of solid phase
HF	AgF	HF	AgF	
0·10	37·72	0·09	50·35	$AgF·4H_2O$
2·07	39·64	1·00	52·15	$AgF·4H_2O$
3·51	40·77	1·64	52·24	$AgF·4H_2O$
4·87	43·27	2·26	54·64	$AgF·4H_2O$
6·43	48·65	3·67	54·97	$AgF·4H_2O$
6·46	48·74	3·55	55·29	$AgF·4H_2O$
7·60	59·85	2·75	71·50	$AgF·2H_2O$
8·20	62·92	6·85	65·99	$AgF·2H_2O$
10·97	61·69	10·19	63·86	AgF
14·00	62·51	12·92	66·31	AgF
17·77	59·87	14·88	73·93	AgF and AgF·HF
19·18	57·95	18·07	63·78	AgF·HF
22·77	53·96	21·68	61·01	AgF·HF
31·35	44·06	26·81	54·79	AgF·HF
41·08	46·14	27·19	66·53	AgF·HF
43·65	44·60	27·66	67·05	AgF·HF
47·02	41·06	35·10	60·04	AgF·HF and AgF·3HF
57·26	30·51	38·70	57·51	AgF·3HF
57·58	31·77	39·60	57·41	AgF·3HF
62·32	27·99	44·31	52·97	AgF·3HF and AgF·5HF
66·36	27·14	45·35	55·05	AgF·5HF
Liquid HF[6]	27·60	—	—	—

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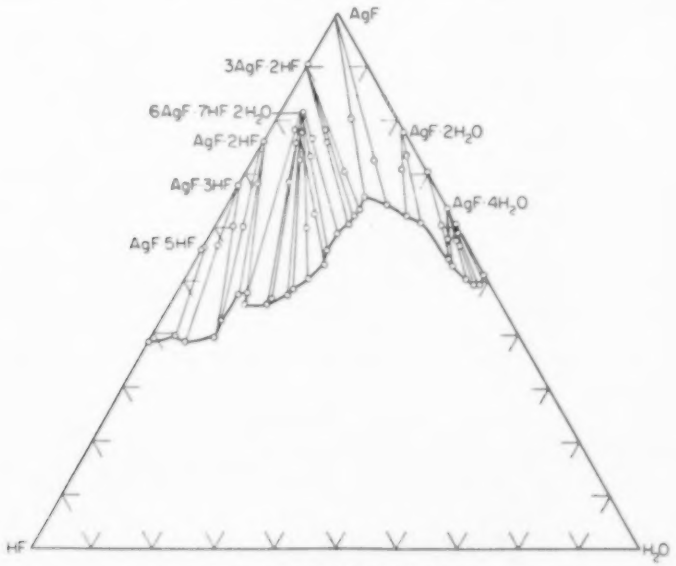

FIG. 1.—AgF–HF–H_2O at 0°.

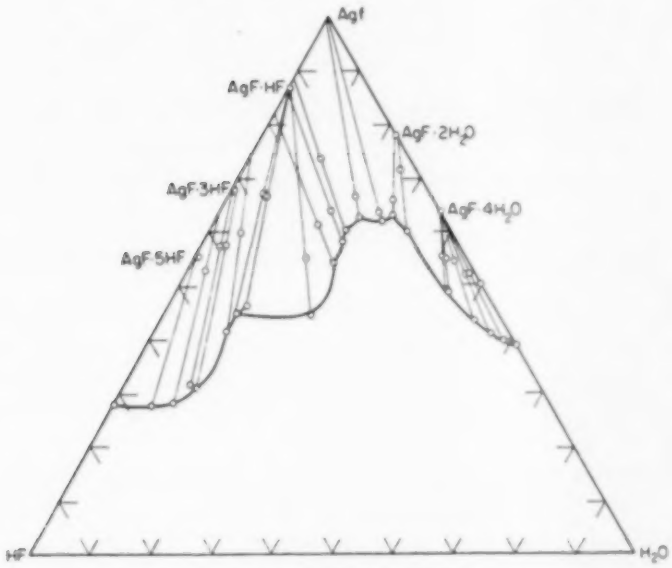

FIG. 2.—AgF–HF–H_2O at −15°

cent) concentration limits for these solid phase are approximately: $AgF{\cdot}4H_2O$, 0–4·5; $AgF{\cdot}2H_2O$, 4·5–7·5; AgF 9·5–12·5; $3AgF{\cdot}2HF$, 14·5–18; $6AgF{\cdot}7HF{\cdot}2H_2O$, 20–42; $AgF{\cdot}2HF$, 42–47·5; $AgF{\cdot}3HF$, 50–55·5%. It is likely that above 55·5 per cent the solid phase is $AgF{\cdot}5HF$. At −15° the solid phases are AgF, $AgF{\cdot}2H_2O$, $AgF{\cdot}4H_2O$, $AgF{\cdot}HF$, $AgF{\cdot}3HF$ and $AgF{\cdot}5HF$. The HF concentration limits for these phases are, $AgF{\cdot}4H_2O$, 0–6·5; $AgF{\cdot}2H_2O$, 7·5–8·5; AgF, 10·5–18; $AgF{\cdot}HF$, 18–47·0; $AgF{\cdot}3HF$ 47·0–62%. Above 62·5 per cent the solid phase is presumed to be $AgF{\cdot}5HF$. In general the solubility of silver fluoride is greater at the higher temperature. It is also more soluble in water than in HF. GUNTZ[3] has reported the eutectic mixture of AgF with H_2O freezes at −14·2°C. This investigation shows that at −15°C the presence of 0·1% HF will break this mixture.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—V*

THE HYDROLYSIS OF SELENIUM

E. SCHULEK and E. KÖRÖS
Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest

(*Received* 20 *March* 1959; *in revised form* 6 *July* 1959)

Abstract—The reactions of selenium with water, with alkali hydroxides and with ammonium hydroxides were investigated. The reactions of selenium with alkali hydroxides and ammonium hydroxide afford colloidal selenium solutions. The experimental evidence was supported by theoretical considerations, on the basis of redox potentials.

IN one of our earlier communications[1] we discussed in detail the hydrolysis of sulphur. The reaction between sulphur and water primarily yields hydrogen sulphide and sulphoxylic acid whilst primarily polysulphide and thiosulphate form in the reaction between sulphur and alkali hydroxides. However, this polysulphide is only an intermediate and, in the further course of hydrolysis, disproportionates into hydrogen sulphide and thiosulphate.

It seemed to be of interest to examine whether a similar hydrolysis also occurs with selenium, and to determine which products form in the reactions between selenium and water, alkali hydroxide and ammonium hydroxide, respectively.

This problem has been relatively rarely discussed in the literature and the statements are rather contradictory.

According to SCHULZE,[2] red selenium is soluble in water whilst in the investigations by JANNEK and MAYER,[3] amorphous selenium proved to be completely insoluble in water. Reaction to a slight extent has been observed at 160° by CROSS and HIGGIN.[4] In the opinion of MONTAGNIE,[5] freshly precipitated red selenium probably reacts with water over 50° as follows:

$$Se + 2H_2O = SeO_2 + 2H_2 \quad (1)$$

Grey selenium was not attacked by water at 160°.

BERZELIUS[6] was the first to study the reactions between selenium and alkali hydroxides and observed that on boiling selenium and concentrated potassium hydroxide, a dark brown solution of potassium selenide was formed. On investigating the rate of reaction between potassium hydroxide and selenium, ESPIL[7] established the following equation:

$$6KOH + (2n + 1)\,Se = 2K_2Se_n + K_2SeO_3 + 3H_2O \quad (2)$$

* Part I: *Z. Anal. Chem.* **139**, 20 (1953); Parts II, III, IV: *Talanta* **3**, 23, 27, 31 (1959).

[1] E. SCHULEK, E. KÖRÖS and L. MAROS, *Acta Chim. Hung.* **10**, 291 (1956).
[2] H. SCHULZE, *J. Prakt. Chem.* **32**, 390 (1885).
[3] J. JANNEK and J. MEYER: *Z. Anorg. Chem.* **83**, 69 (1913).
[4] C. F. CROSS and A. HIGGIN: *J. Chem. Soc.* **35**, 249 (1879).
[5] E. MONTAGNIE, *Bull. Soc. Chim. Fr.* (5) **1**, 507 (1934).
[6] J. J. BERZELIUS, *Lehrbuch der Chemie* (3rd Ed.), Vol. 3, p. 26. Dresden-Leipzig (1834).
[7] R. L. ESPIL, *Bull. Soc. Chim. Fr.* (4) **7**, 155 (1910).

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The same results were also obtained by CALCAGNI.[8] The problem was most thoroughly examined by ADAMI.[9] According to his investigations, which will critically be discussed by us later, the reaction of sodium hydroxide and selenium affords selenide, selenite and selenoselenate $Se_2O_3^{2-}$.

According to BERZELIUS[6] and GORE,[10] no reaction takes place between selenium and ammonium hydroxide whilst CALCAGNI[8] observed that selenium dissolves to a minute extent.

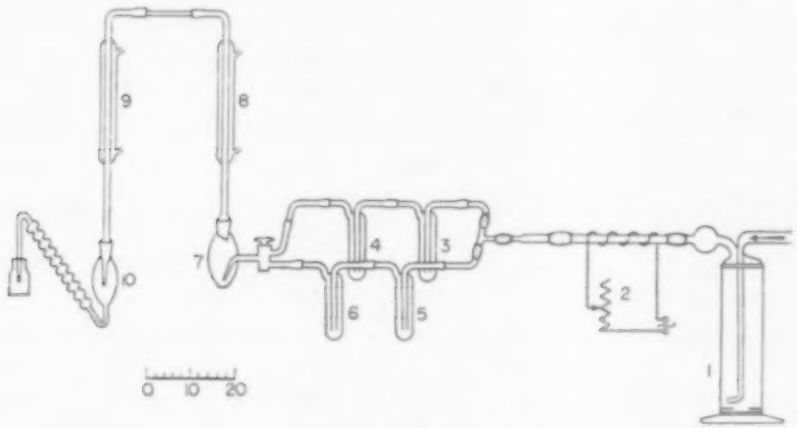

FIG. 1.

EXPERIMENTAL

1. *Reaction of selenium and water*

The only equation known for the reaction between selenium and water originates from MONTAGNIE.[1] It does not seem probable that selenium would be capable of producing hydrogen from water at the low temperature applied. On repeating these experiments, we used a gas buret to collect any hydrogen formed on heating. Our experiments with amorphous selenium, crystalline red selenium and grey selenium proved that, in the absence of oxygen, selenium does not react with water at 100°C. We did not detect any of the reaction products suggested by MONTAGNIE. However, in the presence of air, boiling amorphous selenium with water yielded minute quantities of selenous acid.

It was rather difficult to study the hydrolysis, since amorphous selenium of high reactivity quickly converts into grey selenium at 100°. Accordingly, the reaction, if it existed at all, would soon come to an end. Therefore, it seemed necessary to "stabilize" red selenium in a satisfactory way. For this purpose, we prepared first selenosulphide $(SSe_x)^{2-}$ from sodium sulphide and selenium, since loosely bound selenium does not quickly convert into grey selenium on boiling. On boiling the solution for several hours in a nitrogen current, the presence of selenium was detected in the absorption tube which served as receiver.

2. *The reaction of selenium and alkali hydroxides*

The apparatus shown in Fig. 1. was connected with a cylinder of nitrogen. Traces of oxygen were removed from the gas by traps (1) and (2) containing an alkaline solution of ditionite in pyrogallol and manganese (II) oxide[11] respectively. Trap (3) remained empty whilst 10 ml of a 2 per cent solution of potassium cyanide was placed in trap (4), and traps (5) and (6) each contained 10–15 ml of water.

[8] G. CALCAGNI, *Gazz. Chim. Ital.* **53**, 114 (1923).
[9] P. ADAMI, *Atti Mem. R. Acad. Sci. Lettere Arti Padova, Mem. Cl. Sci. fisico-mat.* **51**, 13 (1934/35).
[10] G. GORE, *Proc. Roy. Soc.* **20**, 441 (1872).
[11] E. SCHULEK and E. PUNGOR, *Mikrochim. Acta* **7–8**, 1116 (1956).

These traps were connected with the reactor flask (7) which contained the weighed sample of selenium (ca. 0·1 g) and some solid sodium or potassium hydroxide (ca. 2 g) in a glass flask which was easily inverted. Two condensers (8, 9) and a ten-ball absorption tube filled with dilute sodium hydroxide (01) were attached to the reactor flask.

A nitrogen current was passed through the apparatus for 30 min, in order to remove air, and then water was introduced into the reactor flask by turning over trap (6). On boiling the reaction mixture for several minutes, selenium completely dissolved, yielding a dark red solution. On allowing this solution to cool in a nitrogen current, trap (4) was inverted, and the solution of potassium cyanide added to the reactor flask (7).†

TABLE 1

Alkalihydroxide	Weighed Se (mg)	Consumed ml of 0·01 N $Na_2S_2O_3$		Found mg of Se/100 ml	
		for Se^{0}*	for Se^{+IV}*	Se^{0}	Se^{+IV}
NaOH (ca. 2 g)	120·4	6·08 6·08 6·07 6·05	0·10 0·13 0·12 0·12	119·8₃	0·24
KOH (ca. 2 g)	110·0	5·56 5·54 5·55 5·55	0·09 0·06 0·07 0·05	109·5₆	0·14

* From the solution diluted to 100 ml 2·00 ml was taken out for Se^{0} determination and 10·00 ml for Se^{+IV} determination.

The reaction took place instantaneously and the solution became colourless. The contents of the reactor flask were transferred into a 100 ml measuring flask and made up to volume with distilled water previously boiled and cooled. The analysis was carried out as follows;

Estimation of Se^{0}[12]. To an aliquot portion of the solution 0·5 g boric acid was added and it was diluted to 60–70 ml. The solution was boiled for 10 min to expel the excess of cyanide and after cooling the pH was adjusted to 3·5–4·0 with dilute perchloric acid. Bromine water was added to the solution to give a permanent yellow colour and the excess of bromine was taken up with 5 ml of 5 per cent phenol. 2 ml of 20 per cent perchloric acid and 0·1 g of potassium iodide were added and after 20 min the iodine was titrated with 0·01 N sodium thiosulphate-solution.

Estimation of $Se^{+IV}(SeO_3^{2-})$. To another aliquot portion of the solution solid potassium hydrogen carbonate, 10 ml of conc. hydrochloric acid and 2 g of potassium iodide were added. Iodine was measured with 0·01 N sodium thiosulphate solution.

Estimation of $Se^{-II}(Se^{2-})$. Another aliquot portion of the solution was pipetted into a distillation flask and 10 ml of 2 N sulphuric acid were added to it. The solution was boiled for 15 min and dilute sodium hydroxide solution was used for the absorption of hydrogen selenide. No traces of selenide were found.

The results are summarized in Tables 1 and 2.

The reaction of selenide and selenite was studied in detail. Sodium selenide was prepared by the absorption by sodium hydroxide of hydrogen selenide formed by the hydrolysis of aluminium selenide. The solution obtained was poured on to sodium selenite in an apparatus free from oxygen (sodium selenite was in a small excess). The analysis of the resulting red solution proved only the presence of elementary selenium and the excess of selenite.

† The reaction should be carried out in a nitrogen current because selenium of a high degree of dispersity quickly oxidizes in air. However, selenocyanide is not attacked by molecular oxygen.

[12] E. SCHULEK and E. KÖRÖS, *Z. Anal. Chem.* **139**, 20 (1953).

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3. *Reaction of selenium and ammonium hydroxide*

The experiments were carried out with (a) amorphous red selenium, (b) crystalline red selenium and (c) grey selenium.

Samples of 100–150 mg of selenium and about 3 ml of concentrated ammonium hydroxide solution were transferred into sealed tubes of about 4·0–4·2 ml volume. The introduction of these substances completely removed air from the tube. After sealing the open ends of the tubes, they were heated in a furnace to 240° and kept at this temperature for 1 hr. The tubes were examined on cooling. In the cases (a) and (b), the solution turned slightly red whilst in case (c) it remained colourless.

After opening the tubes, 1–2 ml of 2 per cent potassium cyanide was added to the solutions. The unreacted grey selenium was filtered off and the solution was transferred to a 100 ml volumetric flask.

The estimation and detection of Se^0, Se^{+IV} and Se^{-II}, respectively, were carried out as described above. Some tenth of a mg of Se^0—as a colloidal solution—was found in the tubes. Neither Se^{+IV}, nor Se^{-II} could be detected.

TABLE 2

Alkali hydroxide	Selenium compound formed (%)		
	Se^{-II}	Se^0	Se^{+IV}*
NaOH	0	99·8	0·2
KOH	0	99·9	0·1

* The presence of some tenth per cent of selenite is probably due to traces of oxygen which entered the system. On carrying out the reaction in air, the reaction mixture contained 92–93 per cent of Se^0 and 8–7 per cent of Se^{+IV}, no Se^{-II} being detectable.

DISCUSSION

1. *Reaction of selenium and water*

According to our experiments selenium reacts with water only to a small extent and therefore the exact identification of the selenium compound causes great difficulties.

It seems possible, however, that the compound distilling is hydrogen selenide and the hydrolysis of selenium can be written:

$$3Se + 3H_2O \rightleftharpoons 2H_2Se + H_2SeO_3 \qquad (3)$$

Results obtained for the alkali hydrolysis of selenium support this assumption. (See below.)

2. *Reaction of selenium with alkali hydroxides*

It appears from the previously given survey of the literature that the dissolving of selenium in alkali hydroxides is considered to be analogous to the dissolving of sulphur. However, with the exception of ADAMI, the method of analysis of the reaction products is not given by the authors.

According to ADAMI,[9] 96·18 per cent of polyselenide, 3·77 per cent of selenite and 0·45 per cent of selenoselenate ($Se_2O_3^{2-}$) form, in the sense of the reaction schemes:

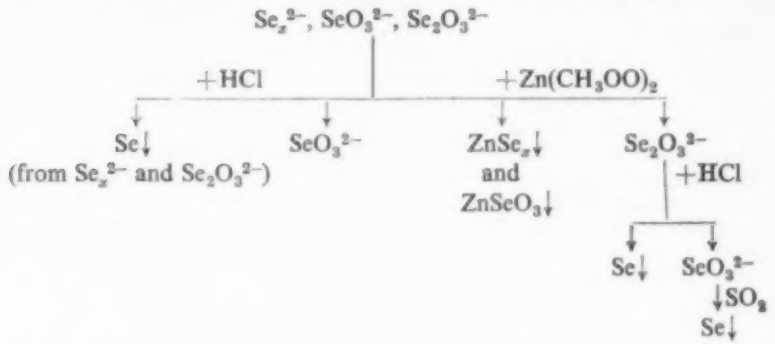
$$2Se + 2H_2O \rightleftharpoons Se^{2-} + SeO_2^{2-} + 4H^+ \qquad (4a)$$

$$3SeO_2^{2-} = Se^{2-} + 2SeO_3^{2-} \qquad (4b)$$

$$Se^{2-} + nSe = Se_{n+1}^{2-} \qquad (4c)$$

$$SeO_3^{2-} + Se \rightleftharpoons Se_2O_3^{2-} \qquad (4d)$$

The analysis method used by ADAMI may be presented schematically:



However, there are some errors in the course of the analysis followed by ADAMI.

1. On acidifying, not only elementary selenium but also hydrogen selenide should form from polyselenide. Hydrogen selenide is not mentioned at all by ADAMI.

2. The course of analysis given by ADAMI does not unequivocally prove the existence of the presumed selenoselenate /$Se_2O_3^{2-}$/*. Thus, selenite and polyselenide may not be precipitated quantitatively by zinc acetate, and the precipitation of selenium on subsequent acidification may be explained in this way.

3. The dissolving of selenium by alkali hydroxides is a disproportionation in the true sense, and identical quantities of oxidation and reduction products should form. However, the analytical data of ADAMI disclose that either the reduction products are in excess or the ratio Se_x/Se^{2-} has a value of 88·6/7·6 = 11·7 which seems to be quite improbable.

4. It must be noted as well that the polyselenideselenium forms in the reaction in a highly dispersed state and is readily oxidized by atmospheric oxygen. Consequently, conclusions as regards the course of the reaction can only be drawn from experiments conducted in a medium completely free of oxygen.

The course of the reaction between selenium and alkali hydroxide or ammonium hydroxide (this latter reacts only at high temperature and pressure) is presumably as follows. Selenium reacts with hydroxyl ions to afford selenide and selenite:

$$3Se + 6OH^- \rightleftharpoons 2Se^{2-} + SeO_3^{2-} + 3H_2O \qquad (5)$$

Selenide and selenite immediately react with each other, with the formation of colloidal red selenium. Our analytical results proved that red selenium in a highly disperse form is the sole product of these reactions. The assumption that both selenide and selenite occur in the end products of the reaction seems incorrect. It is important to note that under the conditions investigated by us ($t_{max} = 240°$, $p_{max} = 30$ atm) grey selenium did not react with ammonium hydroxide.

On carrying out the reaction with barium hydroxide the process described by equation (5) is not completely shifted in the sense of the lower arrow, due to the slight solubility of barium selenite, and the presense of selenide could be detected.

$$3Ba(OH)_2 + (2x + 1)Se = BaSeO_3 + 2BaSe_x + 3H_2O \qquad (6)$$

* Selenoselenate is called hyposelenite by ADAMI; our efforts to prepare sodiumselenoselenate from sodiumselenite and selenium were unsuccessful.

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This interpretation of the reaction can be supported by a knowledge of the redox potentials.

Considering the redox potentials of the partial reactions:

$$Se^{2-} = Se + 2e \qquad E_0 = -0{\cdot}92\ V^{(13)}$$

and,

$$Se + 6OH^- = SeO_3^{2-} + 3H_2O + 4e \qquad E_0 = -0{\cdot}37\ V^{(13)}$$

then, combining both equations:

$$2Se^{2-} + SeO_3^{2-} + 3H_2O = 3Se + 6OH^-$$

$$K = \frac{[Se]^3\,[OH^-]^6}{[Se^{2-}]^2\,[SeO_3^{2-}]}$$

Taking the concentrations of selenium and of hydroxyl ions equal to unity,

$$K = \frac{1}{[Se^{2-}]^2\,[SeO_3^{2-}]}$$

$$E_{0_{SeO_3^{2-}}} + 0{\cdot}015 \log \frac{1}{[Se^{2-}]^2} = E_{0_{Se^{2-}}} + 0{\cdot}015 \log [SeO_3^{2-}]$$

from this

$$[Se^{2-}]^2\,[SeO_3^{2-}] = 10^{-36{\cdot}6}$$

Thus, equation (5) completely shifts in the direction of the lower arrow.

It is of interest to compare the reactions of sulphur and of selenium, respectively, with alkali hydroxides and ammonium hydroxide:

(a) when sulphur is dissolved by alkali hydroxides and by ammonium hydroxide, the primarily formed sulphoxylate or sulphite quickly converts into thiosulphate. In contrast to that, selenite is not capable of further conversion;

(b) in an alkaline solution, sulphide is not oxidized by sulphite whilst selenide is oxidized by selenite, giving the precipitation of elementary selenium. Consequently, the hydrolysis of sulphur and selenium in alkaline solutions are not analogous reactions.

[13] M. M. LATIMER, *The Oxidation States of the Elements* pp. 82–83. McGraw-Hill, New York (1946).

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 64 to 72. Pergamon Press Ltd. Printed in Northern Ireland

THE ANODIC OXIDATION OF ZINC AND CADMIUM IN AQUEOUS SOLUTION

D. T. SORENSEN,* A. W. DAVIDSON and J. KLEINBERG
Department of Chemistry, University of Kansas, Lawrence, Kansas

(*Received* 6 *July* 1959)

Abstract—In the absence of oxidizing agents in the electrolyte solution, only the bipositive ions are formed at zinc and cadmium anodes on electrolysis. In the presence of certain oxidizing agents (e.g. nitrate ion), however, both metals dissolve anodically with an initial mean valence number between one and two; in the presence of chlorate ion zinc dissolves with an initial mean valence number between one and two, whereas cadmium exhibits an initial mean valence number of two. In those solutions in which the initial mean valence number of the metal is less than two, its value decreases further with increasing temperature of electrolysis. No unipositive ion of zinc or cadmium could be isolated, and flow experiments indicated that if the unipositive ion is formed it has a very short lifetime with respect to further oxidation to the bipositive state. All of the experimental data can be explained, however, on the hypothesis that the primary anode reaction is the formation of the unipositive ion, which can then be oxidized to the bipositive state either electrolytically or by an oxidizing agent in the solution. The second oxidation can be thought of as competitive between the oxidizing agent and the electrode. This hypothesis is supported by the relation between the initial mean valence number and the quantity of reduced electrolyte in the anolyte solution.

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THE discrepancy between observed and theoretical quantities of metal dissolved in the course of anodic oxidation was first noted over a hundred years ago, when WÖHLER and BUFF[1], reporting on the anodic oxidation of aluminium in aqueous sodium chloride solutions, noted a current efficiency of 125%. In the notation used in earlier papers from this Laboratory,[2–5] in which the initial mean valence number (V_i) is defined as the number of faradays of electricity required to dissolve anodically one gramme atom of the anode metal, this current efficiency corresponds to a V_i value of 2·40.

As early as 1911 WHITE[6] reported that the "percentage current efficiency" of cadmium anodes in aqueous nitrate solutions was often greater than 100%, on the assumption of the commonly accepted valence of two for the metal. On the other hand, he found that in most of the electrolytes tested in aqueous solution the current efficiency for the zinc anode, on the same basis, was approximately 100%. Sodium nitrate solutions, in sharp contrast to the results to be reported in the present paper, were generally found to yield values of *less* than 100%. WHITE's results, however, were by no means reproducible, ranging from a percentage current efficiency of 80·0% to one of 109·8% for five trials. The main reason for these anomalous results is believed to lie in the fact that he was unable completely to remove the coating which was formed on the anode during electrolysis.

* Present address: The Principia College, Elsah, Illinois.

(1) F. WÖHLER and H. BUFF, *Liebigs Ann.* **103**, 218 (1857).
(2) R. L. PETTY, A. W. DAVIDSON and J. KLEINBERG, *J. Amer. Chem. Soc.* **76**, 363 (1954).
(3) E. RAIJOLA and A. W. DAVIDSON, *J. Amer. Chem. Soc.* **78**, 556 (1956).
(4) B. D. LAUGHLIN, J. KLEINBERG and A. W. DAVIDSON, *J. Amer. Chem. Soc.* **78**, 559 (1956).
(5) A. W. DAVIDSON and F. JIRIK, *J. Amer. Chem. Soc.* **72**, 1700 (1950).
(6) G. R. WHITE, *J. Phys. Chem.* **15**, 723 (1911).

DEL BOCA[7], studying the anodic oxidation of various metals in liquid ammonia, reported that in several instances, including those of a zinc anode with a zinc nitrate electrolyte and a cadmium anode with either a cadmium iodide or a cadmium nitrate electrolyte, less than one farad of electricity was required to dissolve anodically one gramme equivalent of metal. He concluded that a portion of the anode is dissolved as atoms and is transported to the cathode either by electrophoresis or attached to normal divalent ions. In the latter case ions such as $Cd{\cdot}Cd^{2+}$ were postulated. DEL BOCA, then, specifically rejected the hypothesis that the metal could dissolve as a unipositive ion.

More recently, EPELBOIN[8,9] has reported that the valence number of zinc ion in the course of electrolytic polishing of zinc in the presence of perchlorate ion in either a glacial acetic acid or an ethyl alcohol medium is 1·4; this same value was obtained both from the weight of zinc dissolved anodically and from the amount of chloride ion formed from the reduction of the perchlorate ion by the unipositive zinc ion.

Further instances of low valence states attained as products of anodic oxidation in aqueous solutions are presented in several articles from this Laboratory,[2,3,4] in which are postulated, respectively, unipositive magnesium, aluminium, and beryllium ions. The work presented in the present paper continues the method of investigation described in these articles to include zinc and cadmium.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in a typical run consisted of an electrolytic cell, a silver coulometer, a variable voltage full-wave mercury tube rectifier, and an ammeter, all connected in series. All electrolyses were carried out under an atmosphere of nitrogen, from which trace impurities of oxygen had been removed by means of an oxygen absorption train containing metallic copper supported in an ammoniacal solution of copper(I) chloride and ammonium chloride. The electrolytic cell was immersed in a water bath capable, with the aid of additional heaters, of holding the temperature constant to within $\pm 0{\cdot}5°$ from room temperature to 95°C.

The electrolytic cell, similar to the one described by DAVIDSON and JIRIK[3], consisted of individual anode and cathode compartments separated by a sintered glass disk which prevented mixing of the anolyte and catholyte solutions, so that it was possible to make a chemical analysis of the anolyte solution at the conclusion of a run.

In each experiment a current of about 0·1 A was allowed to pass through the electrolyte in this cell, usually for 15 min, and the loss in weight of the anode resulting from electrolytic dissolution and the gain in weight of the coulometer resulting from electrodeposition of silver were determined. A convenient means of tabulating the results is in terms of the initial mean valence number (V_i) which is defined above and can be expressed by means of the equation

$$V_i = \frac{\text{wt of Ag deposited} \times \text{at. wt. of anode metal}}{107{\cdot}88 \times \text{loss in weight of anode}}$$

With both zinc and cadmium, the nature of the surface of the anode was found drastically to affect the V_i values. It was further found that satisfactory cleaning could be accomplished and reproducible results obtained in the case of zinc by immersion in 6 M hydrochloric acid for a few seconds, and in the case of cadmium by immersion in concentrated hydrochloric acid for a few minutes. After the anode had been thus cleaned it was rinsed with water and dried with acetone before the initial weighing. After the completion of a run it was necessary again to clean the anode in such a manner as selectively to remove any coating without dissolving the metal. It was found that this could be effected for zinc anodes by immersion in a deaerated sodium cyanide solution for about a minute, followed by wiping with a paper towel. Cadmium anodes were usually immersed in a Versene solution for several hours;

[7] M. C. DEL BOCA, *Helv. Chim. Acta* **16**, 565 (1933).
[8] I. EPELBOIN, *Z. Electrochem.* **59**, 689 (1955).
[9] P. BROUILLET, I. EPELBOIN and M. FROMENT, *C.R. Acad. Sci., Paris* **239**, 1695 (1954).

under some conditions, however, they could be cleaned by immersion in such a solution for a few minutes only. In each case a blank run was made in which immersion in the electrolyte and cleaning were duplicated as closely as possible but without the passage of an electric current. In order to correct for the nonelectrolytic dissolution which often occurred to a slight extent, the weight loss of the control was deducted from the weight loss of the anode.

In most of the experiments, the quantity of electricity passed was about 0·001 F. The current density was about 0·1 A/cm² for zinc, and about 0·05 A/cm² for the somewhat larger cadmium anodes. Since the results appeared to be little influenced by current density, no attempt was made to measure current densities precisely.

The zinc used was Mallinckrodt "Analytical Reagent," which is reported to contain no more than 0·01 per cent of iron or lead. In some cases in which anomalously low V_i values were observed, the anodes showed one or more visible spots on the surface after electrolysis; in all such cases the anode was discarded. The cadmium anodes were cut from sticks of Baker's "Analysed Reagent" reported to contain no more than 0·03 per cent of zinc. There was no evidence of any localized impurities such as sometimes seemed to be present in the zinc. The various electrolytic solutions were all prepared from reagent grade chemicals.

Each result reported in this paper is the mean of at least three determinations with an average deviation usually within 0·03 V_i unit.

RESULTS

Initial mean valence number in various electrolytes

Under the experimental conditions outlined above, the initial mean valence number of zinc in the presence of the following electrolytes, both at room temperature and at 90°C, was two or very nearly two: 0·2 M solutions of NaCl, KCN, Na_2SO_4 and K_2CrO_4, and 5·0 M NaCl. In certain cases the V_i number was slightly greater than two, a fact which seems to indicate overcorrection for nonelectrolytic corrosion. Cadmium exhibited an initial mean valence number of two not only in these same solutions but also in 0·2 M $KClO_3$; in the latter medium, however, zinc entered solution with an initial mean valence number less than two. In no case was there observed any evolution of gas from the anode; in this respect the behaviour of zinc and cadmium differs markedly from that of magnesium, beryllium and aluminium.[2,3,4]

In sodium nitrate solutions both zinc and cadmium exhibited initial mean valence numbers notably *less* than two; these values were found to be largely dependent on temperature, and to a slight extent also on concentration, lower values being obtained at higher concentrations or higher temperatures. The values of the initial mean valence number of zinc in 0·2 M $NaNO_3$ and in 0·2 M $KClO_3$ as a function of temperature are shown in Fig. 1, and of cadmium in 0·2 M $NaNO_3$ as a function of temperature in Fig. 2. The variation of V_i values of cadmium with concentration of sodium nitrate at 30° is shown below.

Concentration (M)	0·2	0·9	2·5	5
V_i	1·55	1·54	1·48	1·37

As a step toward the elucidation of the mechanism of the anodic oxidation process, V_i values were determined for mixtures of electrolytes under various conditions. The results for zinc and cadmium anodes in sodium nitrate–sodium chloride mixtures are shown in Figs. 3–4, and those for a few other electrolytic mixtures are listed in Table 1.

Correlation of the initial mean valence number as calculated by two different methods

If, as proposed in a previous paper,[2] the mechanism of anodic oxidation of an active metal consists in primary electrolytic oxidation to the unipositive state followed

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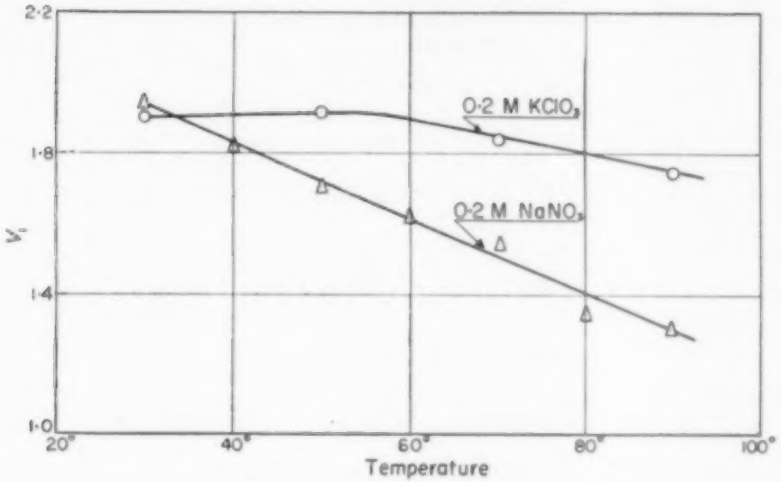

FIG. 1.—Effect of temperature on V_i value of zinc.

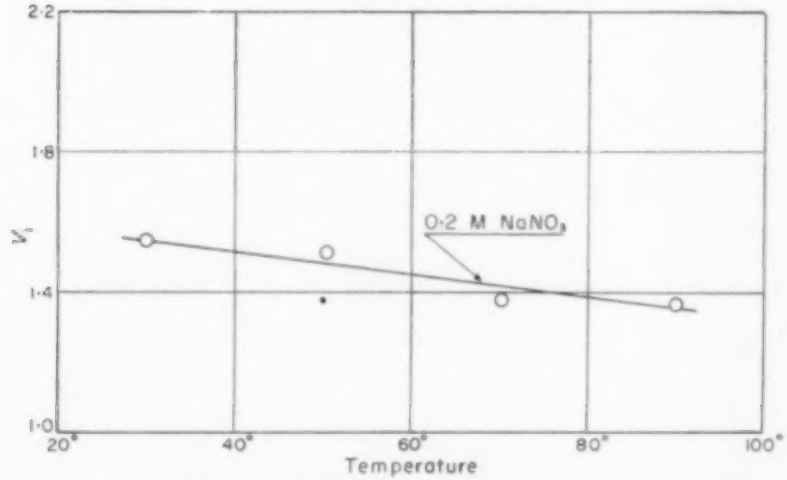

FIG. 2.—Effect of temperature on V_i value of cadmium.

by oxidation to the normal oxidation state as a second step, it should be possible to correlate the amount of reduced anolyte with the initial mean valence number as calculated from the loss in weight of the anode and coulometric data. An equation relating the number of gramme equivalents of electrolyte reduced and the weight of silver deposited in the coulometer with the initial mean valence can readily be derived:

$$V_i = \frac{2 \times \text{wt. of Ag deposited}}{\text{wt. of Ag deposited} + 107{\cdot}88 \times \text{no. of gramme equivalents of reduced electrolyte}}$$

The number of gramme equivalents in this case is defined as the number of moles of reduced substance formed multiplied by the change in oxidation number suffered by the electrolyte upon reduction.

TABLE 1.—V_i VALUES FOR ZINC IN VARIOUS MIXTURES AT 30°

Electrolytes	Concentration (M)	V_i
NaCl	2·50	1·77
$NaNO_2$	0·20	
KCN	0·20	1·99
$NaNO_3$	0·20	
NaCl	2·50	2·02
Na_2SO_4	0·20	
NaCl	2·50	2·02
$KClO_3$	0·20	

Anodic oxidation runs were performed in exactly the same manner as those reported earlier in this paper, except that the electrolyses were carried out for a longer period of time in order to increase the quantity of reduced substance in the anolyte, and a chemical analysis was made of the anolyte solution.

In one such experiment, the amount of nitrite formed in the anolyte upon electrolysis at 60°C with a zinc anode and an electrolyte of 0·2 M sodium nitrate solution was determined; in another a similar electrolysis was carried out at 30°C with a cadmium anode; and finally, chloride was determined in the anolyte after electrolysis at 90° with a zinc anode of a 0·2 M potassium chlorate solution. Nitrite ion was determined by titration with a standardized potassium permanganate solution, and chloride by potentiometric titration with silver nitrate solution. The results are shown in Table 2.

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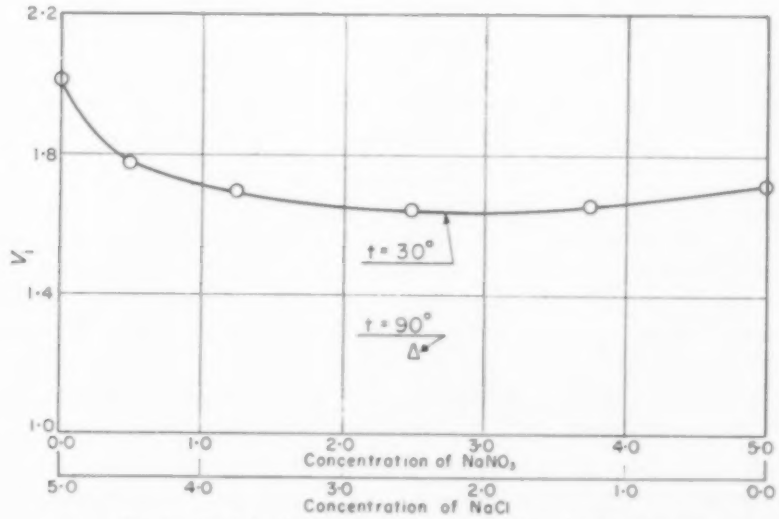

FIG. 3.—V_i of zinc in mixed sodium nitrate–sodium chloride solutions.

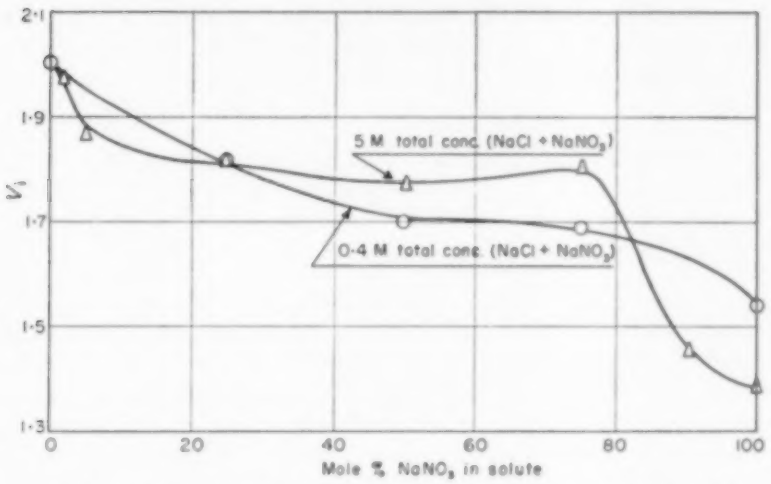

FIG. 4.—V_t of cadmium in mixed sodium nitrate–sodium chloride solutions at 30°.

Reduction at a distance from the anode

By means of the method previously described,[2] an attempt was made to determine whether or not a product was formed in the anodic oxidation of zinc which could effect reduction in a solution not in contact with the anode. In one experiment sodium sulphate as the flowing electrolyte and ammoniacal silver nitrate as the oxidizing agent were used; in another, sodium chloride as the flowing electrolyte and potassium permanganate as the oxidizing agent; and finally sodium chloride as the flowing electrolyte and a ferric chloride–potassium ferricyanide mixture as the oxidizing agent. For each of the three experiments two types of blank runs were made: in one the experiment was carried out just as before but without the passage of an electric current; in the other the solution was electrolysed with an anode of platinum instead of zinc.

In none of the three experiments did the trace amount of reduced substance differ significantly from the trace amount formed in the corresponding blank run; hence the

TABLE 2.—COMPARISON OF V_t VALUES AS DETERMINED BY TWO METHODS

Zn in 0·2 M $NaNO_3$ at 60°		Cd in 0·2 M $NaNO_3$ at 30°		Zn in 0·2 M $KClO_3$ at 90°	
Coulometric data	Reducing power	Coulometric data	Reducing power	Coulometric data	Reducing power
1·57	1·67	1·49	1·51	1·69	1·74
1·66	1·78	1·57	1·55	1·81	1·78
1·60	1·79	1·58	1·56	1·74	1·77
1·67	1·79	1·54	1·56		

results were considered negative. Consequently, it must be concluded that if unipositive zinc ion is formed in the course of anodic oxidation, it has too short a life to be swept away from the anode by a flowing electrolyte.

DISCUSSION OF RESULTS

The results herein described can be accounted for in terms of a two-step mechanism for the anodic oxidation of zinc and cadmium. The first step involves electrolytic oxidation of the metal to the unipositive ion according to the following equation:

$$M \rightarrow M^{+} + e^{-} \tag{1}$$

The unipositive ion thus postulated would be expected to be very reactive and readily to form a bipositive ion. There are two ways in which this second step can occur: one is by further electrolytic oxidation at the anode, the other is by nonelectrolytic oxidation by an oxidizing agent in the solution. The fact that evolution of hydrogen is not observed at the anode indicates that the univalent zinc or cadmium ion is not oxidized by water. Consequently, the second step might be either

$$M^{+} \rightarrow M^{2+} + e^{-} \text{ (at the electrode)} \tag{2}$$

or,

$$M^{+} + \text{oxidant} \rightarrow M^{2+} + \text{reductant (in the solution)} \tag{3}$$

With nonreducible electrolytes reaction (3) cannot occur, and consequently an initial mean valence number of two is observed. With reducible electrolytes, on the other hand, the two possible mechanisms of the second step are competitive; which of them predominates will depend upon the nature of the oxidizing electrolyte, as well as upon the conditions of the experiment. The initial mean valence number might then range from one to two, depending upon the relative extents of the occurrence of reactions (2) and (3), which must in turn depend upon the relative rates of these two reactions. The fact that the V_i number, especially of cadmium, tends to decrease with increasing concentration of oxidant at a given temperature might have been expected, since it is certain that reaction (3) occurs more rapidly as the concentration of oxidant is increased.

Certain electrolytes, such as sodium sulphate and potassium chromate, apparently are not rapid enough oxidizing agents to oxidize unipositive zinc or cadmium to any significant extent in competition with the electrolytic oxidation of the unipositive ion. Potassium chlorate does not appreciably oxidize unipositive cadmium even at 90°, but it does compete with the electrolytic oxidation of unipositive zinc to give somewhat lower V_i values, particularly at higher temperatures (see Fig. 3). In all cases where the change in V_i with temperature is large enough to be significant, the value decreases with increasing temperature (see Figs. 1 and 2). This fact may be accounted for by the supposition that the rate of reaction (3) increases more rapidly with increasing temperature than does that of reaction (2).

As a possible alternative hypothesis, it has been suggested that nonelectrolytic dissolution might occur only under the influence of an anodic current. PETTY *et al.*[2] concluded, in the case of a magnesium anode, that this hypothesis was not likely to be valid, because the same V_i values were obtained with an intermittent current as with a continuous current. Although no such experiments were carried out in the present investigation, yet it seems probable that nonelectrolytic dissolution of zinc or cadmium during the course of electrolysis is *inhibited*, rather than promoted, by the passage of

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an anodic current, because the blank correction was frequently found to be excessive, giving an apparent V_i value greater than two.

Inspection of Fig. 3 reveals that at a temperature of 30° an aqueous solution of a 1 : 1 sodium chloride–sodium nitrate mixture at a total concentration of 5·00 M gives an initial mean valence number for zinc lower than that found for a solution of either salt alone at that concentration. A reasonable explanation of this phenomenon might be that the oxidation of unipositive zinc ion by nitrate ion according to equation (3) is catalysed by chloride ion. It is interesting to note in this connection that the rates of certain electron exchange reactions are greatly increased upon addition of chloride ion. In a recent review article, ZWOLINSKI *et al.*[10] give many references to this phenomenon. LIBBY[11] proposed a catalytic effect based upon the formation of a complex ion containing chloride; whereas TAUBE and his co-workers[12,13,14] proposed a bridge transfer mechanism wherein the added group (e.g. chloride) is co-ordinated between oxidant and reductant to form a "bridge" which serves as a path for the transfer of electrons.

The results of experiments carried out with a cadmium anode in sodium chloride–sodium nitrate solutions of 5·00 M total concentration are considerably different from those observed for a zinc anode. As can be seen from inspection of Fig. 5, no minimum is observed for the value of V_i at any intermediate concentration; rather, a plateau covering a wide range of concentration exists at a V_i value of about 1·8. Even an increase in temperature from 30° to 90° had no more than a negligible effect on the V_i value in a 1 : 1 sodium chloride–sodium nitrate solution of 5·0 M total concentration. No satisfactory explanation of this divergence in behaviour from that observed for zinc can be offered at this time.

In a few other experiments in mixed electrolyte solutions (see Table 1), the results were not unlike what would be expected. It is interesting to note that the V_i value for zinc in a solution 0·2 M with respect to sodium nitrite and 0·2 M with respect to potassium cyanide is approximately 2·0, whereas the V_i value for the same metal in a solution having the same concentration of sodium nitrite but 2·50 M with respect to sodium chloride is 1·77. This is not surprising in view of the fact that cyanide ion is a much more effective complexing agent for bipositive zinc ion than is chloride; the dissociation constant of $ZnCl^+$ is 1·5, whereas that of $Zn(CN)_4^{2-}$ is only $1{\cdot}3 \times 10^{-17}$.[15]

The two-step mechanism hypothesis proposed in equations (1), (2) and (3) receives considerable support from the results of the experiments in which the V_i value determined from the amount of reduced anolyte is compared with the V_i value as determined by the weight loss of the anode. When the V_i values of zinc in sodium nitrate solutions as calculated by the two methods are compared, it is noted that in every case the value determined from the amount of nitrite formed in the anolyte exceeds that determined from the weight loss of the anode. It was suspected that in this case some oxides of nitrogen are lost either during electrolysis or during the titration. This seems probable because experimental runs at even higher temperatures

[10] B. J. ZWOLINSKI, R. J. MARCUS and H. EYRING, *Chem. Rev.* **55**, 157 (1955).
[11] W. F. LIBBY, Abstracts of Papers presented at the 115th Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, San Francisco, California (1949).
[12] H. TAUBE, H. MYERS and R. L. RICH, *J. Amer. Chem. Soc.* **75**, 4118 (1953).
[13] H. TAUBE and H. MYERS, *J. Amer. Chem. Soc.* **76**, 2103 (1954).
[14] H. TAUBE and E. L. KING, *J. Amer. Chem. Soc.* **76**, 4053 (1954).
[15] W. M. LATIMER, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* (2nd Ed.) Prentice Hall, New York (1952).

showed errors in the same direction but of much greater magnitude. On the other hand, the correlation of the V_t values calculated for cadmium in a sodium nitrate solution by the two methods was found to be much closer, probably because a lower temperature could be used. In each of the four trials, the differences in the initial mean valence numbers as determined by the two methods are well within the limits of experimental error.

In view of the lack of positive results on experiments where reduction at a distance from the anode was attempted, it must be concluded that the unipositive ion formed has a life too short to permit its detection after it has been swept away from the anode by a flowing electrolyte. The results suggest that the time interval between reactions (1) and (2) must be very short. No evidence for the evolution of hydrogen at the anode was found under any circumstances in this entire investigation. It is significant that other investigators[2,3,4] not only obtained positive results in flow experiments with magnesium, beryllium and aluminium, but also observed evolution of hydrogen at the anode. Possibly the electrolytic oxidation of unipositive zinc or cadmium to the bipositive ion follows the first step in the electrolytic oxidation by an extremely short time interval, much shorter than for magnesium, beryllium or aluminium, and yet long enough to permit chemical oxidation by the more rapid oxidizing agents, such as nitrate, to compete to a certain extent.

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NITRO COMPLEXES OF NITROSYLRUTHENIUM

P. G. M. BROWN
Atomic Energy Research Establishment, Harwell, Didcot, Berks

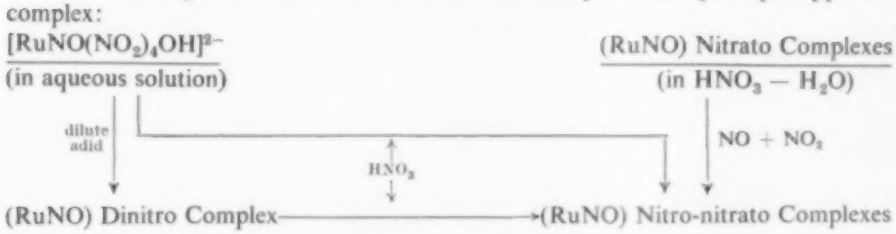
(*Received* 15 *June* 1959)

Abstract—Complexes of nitrosylruthenium or mixtures of these, with the general formula $[RuNO(NO_2)_x(NO_3)_y(OH)_{3-x-y}(H_2O)_2]$ with $x \geq 1$, have been isolated as solids. Of these one, $[RuNO(NO_2)_2OH(H_2O)_2]$, was prepared by the action of dilute acid on $Na_2[RuNO(NO_2)_4OH]$ and two others with empirical formulae $[RuNO{\cdot}NO_2(NO_3)_2(H_2O)_2]$ and $[RuNO(NO_2)_3(H_2O)_2]$, were obtained by evaporation *in vacuo* of solutions formed in nitric acid by the action of oxides of nitrogen ($NO + NO_2$) on (RuNO) nitrato complexes.

The complexes have been identified by quantitative analysis for the various groups present, by infra-red spectroscopy and by paper chromatography. As might be expected of complexes containing the nitro ligand, the formation and interconversion reactions are slower than those of the corresponding (RuNO) nitrato complexes.

FISSION product ruthenium[1,2] occurs in nitric acid solutions of irradiated fissile material largely as the nitrosylruthenium radical (RuNO)III, complexed with nitrato, nitro, hydroxo and aquo ligands. These complexes have aroused considerable interest, and the isolation of some of them has already been reported.[3] This paper deals specifically with the isolation of a dinitromonohydroxy complex, and also discusses the formation of certain other less well defined complexes.

The following scheme shows the inter-relationships of the principal types of complex:



Infra-red spectroscopy has proved valuable for establishing the presence or absence of co-ordinated nitro, nitrito or nitrato groups in these complexes.

EXPERIMENTAL

General

^{106}Ru *labelled preparations.* These were used for paper chromatography and solvent extraction work. ^{106}Ru labelled solutions of (RuNO) nitrato complexes in ~12 M HNO_3, obtained from R.C.C. Amersham, enabled solid preparations[3] of the (RuNO) nitrato complexes to be labelled. These formed the starting material for the new preparations.

[1] J. M. FLETCHER and F. S. MARTIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 141. United Nations (1956).
[2] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. G. WAIN and J. L. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 17, p. 118. United Nations (1959).
[3] J. M. FLETCHER, I. L. JENKINS, F. M. LEVER, F. S. MARTIN, A. R. POWELL and R. TODD, *J. Inorg. Nucl. Chem.* **1**, 378 (1955).

Organic solvents. Tributyl phosphate (TBP) and methyl isopropyl ketone (MIPK) were purified by methods previously described;[4] TBP was employed in the form of a 30 per cent solution in odourless kerosene. Before distribution measurements the organic solvent was always equilibrated with an aqueous phase of relevant composition. An equal volume of the organic phase was added to and stirred with the aqueous phase for 30 sec at 20°C. The ruthenium distribution coefficient, D_{Ru}, was measured as already described.[4]

Paper chromatography. Paper chromatograms were obtained by the method previously described.[4,5] MIPK equilibrated with 3 M HNO_3 was used as the eluting solvent throughout this work.

Analysis

Ruthenium. About 0·015 g of the compound was fused with potassium hydroxide (1 g) and potassium nitrate (1 g) in a nickel crucible, and the potassium ruthenate in the melt was dissolved in 2 M KOH solution at about 50°C. The solution was cooled, made up to 500 ml with 2 M KOH, and analysed spectrophotometrically.

Total nitrogen. The compound was reduced with Devarda's alloy and the liberated ammonia determined.

Nitrosylruthenium group (RuNO). Nitrosylruthenium hydroxide[3] was precipitated by securing the precise conditions necessary for its quantitative separation. From 0·05 to 0·1 g of the compound was dissolved in about 20 ml of 3 M NaOH (pH ~ 12) and the solution was boiled for an hour in order to produce nitrosylruthenium hydroxide in a colloidal form. The solution was cooled and the pH adjusted to 6·4 with perchloric acid to bring down the hydroxide as a flocculent precipitate. This was kept in contact with the mother liquor for about a fortnight to complete precipitation, and was then collected on a weighed sintered glass crucible. The precipitate was washed with water several times, dried at 80°C and weighed. Found for three specimens Ru = 49·3, 49·6 and 49·0%. Previous work[3] has shown that the precipitate obtained under these conditions contains ~49·8% Ru (required for $RuNO(OH)_3 \cdot H_2O$, 50·6% Ru).

Nitro or nitrito group. The filtrate and washings from the analysis for (RuNO) were collected and the nitrite present was determined by oxidation with ceric sulphate.

Nitrato group. The complex was boiled with aqueous caustic soda to release nitrato ligands as NO_3^- ions. The solution was acidified with acetic acid, boiled for a few minutes, and the nitrate precipitated as nitron nitrate at 0°C. When present at concentrations in excess of 2 g/l. the NO_3^- ion is also precipitated with nitron acetate; however, in the present solutions the nitrite ions never exceeded 0·5 g/l.

Infra-red spectra. These were obtained on a Grubb-Parsons double beam infra-red spectrometer, equipped with a S3A monochromator; samples were presented between rock-salt plates as mulls with Nujol and were prepared in a drybox because of the hygroscopic nature of the complexes.

DINITROMONOHYDROXY-NITROSYLRUTHENIUM $[RuNO(NO_2)_2OH(H_2O)_2]$

Preparation

The molecule of sodium tetranitronitrosylruthenate when warmed to about 60°C in dilute acid, loses two of its four nitro groups:[3]

$$[RuNO(NO_2)_4OH]^{2-} \rightarrow [RuNO(NO_2)_2OH(H_2O)_2] + 2NO_2^-.$$

From perchloric acid, the dinitromonohydroxy complex can be isolated after removing sodium and perchlorate ions by means of ion exchange resins. To obtain a good yield, contact with the resin must be of limited duration since there is a slow change of the non-ionic dinitro complex into a charged species. In consequence, equilibration with mixed cation and anion exchange resins at 20°C gives a yield of 50 per cent after 5 min but only 5 per cent after an hour.

[4] J. M. FLETCHER, P. G. M. BROWN, E. R. GARDNER, C. J. HARDY, A. G. WAIN and J. L. WOODHEAD, *J. Inorg. Nucl. Chem.* **12**, 154 (1959).
[5] A. G. WAIN, P. G. M. BROWN and J. M. FLETCHER, *Chem. & Ind.* 18 (1957).

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Sodium tetranitronitrosylruthenate (1 g) was dissolved in about 20 ml of water, and the stoicheiometric quantity of perchloric acid for the reaction was added. The solution was boiled for a few minutes and then held at 100°C for 20 min to complete the reaction and drive off the nitrous fumes as they were produced; during this operation it changed in colour from yellow to orange. After being cooled to room temperature it was subjected in quick succession to three 5 min equilibrations with a large excess of a mixture of the resins De-acidite FF (in OH form) and Zeo-Karb 225 (in H form). After treatment, the absence of perchlorate ions from the solution was shown by adding potassium chloride to a portion. The neutral solution was evaporated *in vacuo* over phosphorus pentoxide to give an orange-brown crystalline solid. (Found: Ru 37·2, RuNO 46·9, N 15·1, NO_2 32·5, NO_3 nil, OH and H_2O (by difference) 20·6. Calc. for $[RuNO(NO_2)_2OH(H_2O)_2]$, mol. wt. 276·8, requires Ru 36·7, RuNO 47·6, N 15·2, NO_2 33·2, OH and H_2O 19·2%).

Properties

Cryoscopic measurements in water (0·0465 g complex in 10 g water) gave the anomalously low figure of 111 for the molecular weight.

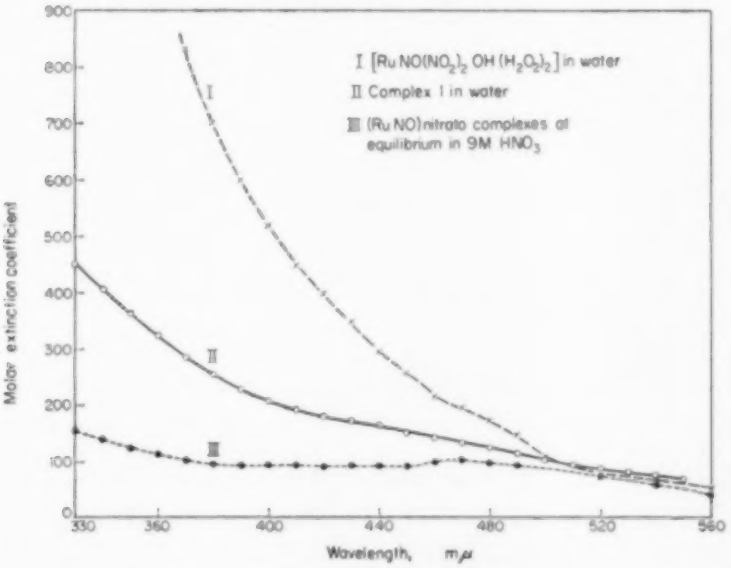

FIG. 1.—Visible absorption spectra of some (RuNO) complexes.

The infra-red spectrum (FLETCHER[6], Fig. 4) of this complex has a strong band at 1873 cm^{-1} arising from the NO stretching frequency of the nitrosyl group. The bands of medium intensity at 1439, 1321 and 825 cm^{-1} are respectively ascribed to the asymmetric stretching, symmetric stretching and deformation vibrations of the nitro ligand.[7] The deformation frequency of the water molecule appears in medium strength at 1610 cm^{-1}, and O—H stretching frequencies are observed at 3322 and 3096 cm^{-1}.

The absorption spectra of freshly-prepared aqueous solutions of this and similar nitro complexes of (RuNO) in the visible region (Fig. 1) show a continuous increase in optical density towards the ultra-violet; in this respect the nitro complexes differ from the nitrato complexes of (RuNO).

Solutions of the complex in water and in nitric acid undergo slow changes which resemble those of the nitrato nitrosylruthenium complexes,[6] e.g. the value of D_{Ru} between 30% TBP and 3 M HNO_3 with 2·5 M $NaNO_3$ falls with time of ageing in the aqueous phase (by factors of 3 and 7 after 3 and 10 days respectively). Paper chromatography has been applied to a $1{\cdot}13 \times 10^{-2}$ M solution of the complex in the course of its ageing at 20°C in 3 M HNO_3 containing excess (0·07 N) ceric sulphate.

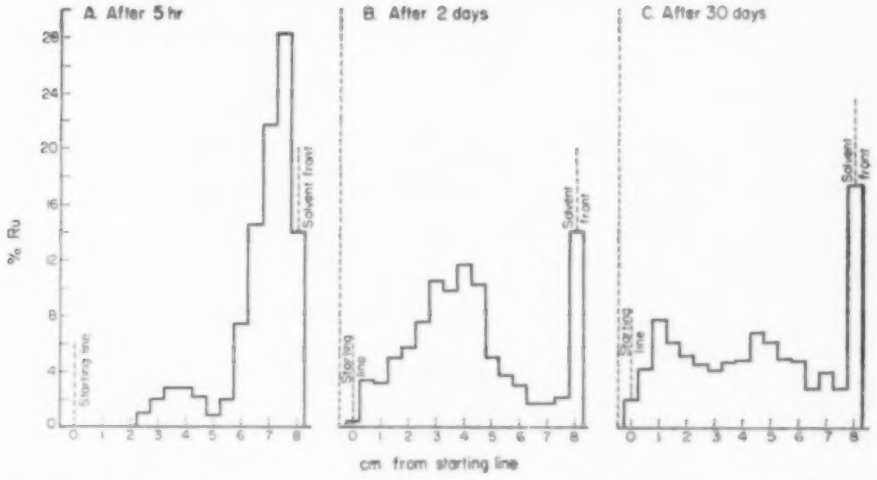

FIG. 2.—Paper chromatograms illustrating the ageing of dinitro nitrosylruthenium in 3 M HNO_3 + excess ceric sulphate.

This has shown that under these conditions

(a) the form of the dinitro complex in nitric acid has $R_F = 0{\cdot}9$ to 1·0 (Fig. 2A);
(b) there is a slow decomposition which gives at least two products (Figs. 2A to 2C).

The results (Table 1) from this experiment indicate that consecutive reactions are taking place:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

A represents the dinitro complex in nitric acid and B and C compounds which may contain respectively one and zero nitro groups per molecule. Values of $k_1 = 0{\cdot}7$ day^{-1} ($t_{1/2} \sim 1$ day) and $k_2 = 0{\cdot}034$ day^{-1} ($t_{1/2} \sim 20$ days) were found. The growth of the peak at the solvent front (Table 1) after ageing for 8 days is consistent with the occurrence of slow nitration reactions which render the final product a mixture of nitro-nitrato and nitrato complexes of nitrosylruthenium.

The complex dissolves in oxygen-containing solvents such as TBP and MIPK. Partition coefficients for solutions made from the solid and aged for less than 5 min in the aqueous phase, a time short enough for hydrolysis to be insignificant, are given in Table 2. The equivalence of the forward and backwash partition coefficients (K) in several experiments shows that one species only is present. Table 2 also shows

[6] J. M. FLETCHER, *J. Inorg. Nucl. Chem.* **8**, 277 (1958).
[7] R. B. PENLAND, T. J. LANE and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **78**, 887 (1956).

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TABLE 1.—THE DECOMPOSITION OF $[RuNO(NO_3)_2OH(H_2O)_2]$ IN 3 M HNO_3 CONTAINING 0·07 N CERIC SULPHATE AT 20°C

$C_{Ru} = 1{\cdot}13 \times 10^{-2}$ M

Time of ageing	NO_3^- liberated: % of total NO_3 in complex	Paper chromatography: % Ru with R_F		
		0·9–1·0	0·25–0·9	0·0–0·25
5 hr	6·0	87·5	12·5	0·0
18 hr	19·7	60·0	32·4	7·6
2 days	37·6	22·0	69·0	9·0
8 days	50·6	9·5	78·5	12·0
14 days	55·5	12·0	67·6	20·4
30 days	63·7	19·8	49·9	30·3

that, as with the (RuNO) nitrato complexes,[4] extractability into TBP solutions decreases as the nitric acid concentration is increased.

The factors governing the formation of the dinitro complex from the tetranitro complex have been discussed in an earlier paper.[3] Since the substitution of weakly bound ligands in the position *trans* to the strongly *trans*-directing nitrosyl group is relatively easy, the hydroxyl in this complex is probably replaced by a nitrato ligand in nitric acid solution.

TABLE 2.—DISTRIBUTION OF $[RuNO(NO_3)_2OH(H_2O)_2]$, AT 20°C FOR 30 sec EQUILIBRATION, BETWEEN CERTAIN ORGANIC SOLVENTS AND FRESHLY PREPARED AQUEOUS NITRIC ACID–SODIUM NITRATE SOLUTIONS

$C_{Ru} \sim 5 \times 10^{-3}$ M

Aqueous phase		Solvent phase	K	
C_{HNO_3} (M)	C_{NaNO_3} (M)		Forward	Backwash*
—	5·0	30% TBP/kerosene	2·20	—
0·1	—	30% TBP/kerosene	2·04	—
1·0	—	30% TBP/kerosene	1·70	1·66
1·0	4·5	30% TBP/kerosene	1·20	—
3·0	—	30% TBP/kerosene	0·506	0·514
3·0	2·5	30% TBP/kerosene	0·215	0·214
—	5·0	MIPK	1·15	—
3·0	2·5	MIPK	1·82	—

* These partition coefficients were obtained by back-washing the solvent phase with the equilibrium aqueous phase with respect to nitric acid and sodium nitrate.

OTHER (RuNO) NITRO COMPLEXES OBTAINED IN THE SOLID STATE

A solid with RuNO : NO_2 : NO_3 = 1 : 1 : 2, e.g. $[RuNO{\cdot}NO_2(NO_3)_2(H_2O)_2]$

Preparation

This solid (Complex I) was formed when oxides of nitrogen (NO + NO_2) were passed through a solution of (RuNO) nitrato complexes in 6 to 8 M HNO_3 at about 50°C.

About 1 g of a solid in which the ratio RuNO : NO_2 equalled 1 : 3 was dissolved in 20 ml of 6 M HNO_3. Oxides of nitrogen, produced by the action of concentrated nitric acid on copper turnings, were passed continuously through the solution for 5 hr at 50°C. In this time the solution

TABLE 3.—INFRA-RED ABSORPTION BANDS ARISING FROM THE "NO" STRETCHING FREQUENCY OF THE NITROSYL GROUP IN (RuNO) COMPLEXES

Complex	NO Stretching frequency (cm^{-1})
$RuNO(OH)_3{\cdot}H_2O$	1838
$[RuNO(NO_3)_2OH(H_2O)_2]$	1873
$Na_2[RuNO(NO_3)_4OH]{\cdot}2H_2O$	1905
$RuNOCl_3$	1916
$K_2[RuNOCl_5]$	1919
Complex I	1931
Nitrato with Ru : NO_3 = 1 : 3	1934
$RuN_2O_{7\cdot5}$	~1935

changed in colour from cherry to brick-red. It was cooled and evaporated *in vacuo* over phosphorus pentoxide and solid sodium hydroxide for a period of several days (under these conditions the nitric acid concentration in the last traces of the mother liquor can reach a value as high as 20 M). The resulting solid was brick-red and glassy. (Found : Ru, 30·3, RuNO, 39·4, N 16·9, NO_2, 13·4, NO_3, 36·6, H_2O (by difference), 10·6. Calc. for $[RuNO{\cdot}NO_2(NO_3)_2(H_2O)_2]$, mol. wt. 337·8; Ru, 30·1, RuNO, 39·0, N 16·6, NO_2, 13·6, NO_3, 36·8, H_2O, 10·6%).

Properties

The depression of the freezing point brought about by 0·1563 g of complex in 10 g of water indicated a molecular weight of 161.

The infra-red spectrum (FLETCHER[6], Fig. 4) of this material shows the NO stretching frequency as a strong band at 1931 cm^{-1} which is considerably higher than in the dinitro complex (1873 cm^{-1}). The presence of OH groups seems to lower the NO stretching frequency; for instance in the trihydroxy complex it is as low as 1838 cm^{-1} (Table 3). Medium intensity bands at 1504, 1276 and 786 cm^{-1} arise from the asymmetric stretching, symmetric stretching and deformation vibrations respectively of the covalently bound nitrato ligand.[8] These, together with the bands due to the organic medium, tend to mask the asymmetric and symmetric stretching frequencies of the nitro ligand in the regions 1430 and 1315 cm^{-1}, but the strong band at 833 cm^{-1} may be identified with the NO_2 ν_2 deformation vibration.[7] Water deformation and O—H stretching frequencies are observed at 1618 and 3597 cm^{-1}

[8] B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM, *J. Chem. Soc.* 4222 (1957).

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respectively. There are two broad bands at 1143 and 989 cm^{-1}; the origin of these is in doubt.[9]

Absorption of the aqueous solution of Complex I in the visible region (Fig. 1) is featureless, except for the usual increase towards the ultra-violet.

The material is soluble in oxygen-containing organic solvents, and is more soluble ($D_{Ru} = 0{\cdot}8$ from 5 M HNO_3) in 30% TBP in kerosene than either the higher nitrato complexes of nitrosylruthenium ($D_{Ru} \sim 0{\cdot}03$) or the dinitro nitrosylruthenium complex ($D_{Ru} \sim 0{\cdot}1$).

The glassy nature of this solid suggests a mixture, either of geometrical isomers with the same empirical formula, or, less likely, of complexes with different empirical formulae especially in the relative number of nitro and nitrato groups. The high value of D_{Ru} into TBP supports the view that this is not a mixture of known nitro and nitrato complexes of (RuNO).

A solid with RuNO : $NO_2 = 1 : 3$, e.g. $[RuNO(NO_2)_2(H_2O)_2]$

Preparation

This solid (Complex II) was made in a similar manner to I, except that the reaction was carried out in 3–5 M HNO_3 and followed by a rapid desiccation of the product *in vacuo*.

A solution of (RuNO) nitrato complexes in 3 M HNO_3 was prepared (cf. I) and heated to 65°C, and oxides of nitrogen were passed through it for periods of 2 min at 15 min intervals for 3 hr. This procedure ensured that, although enough HNO_2 (~0·1 M) remained in solution to meet the requirements of the reaction, the concentration of nitric acid did not rise above 5 M. The original cherry-red colour of the solution changed to orange as the reaction proceeded. The hot solution was placed in a desiccator over phosphorus pentoxide and solid sodium hydroxide, and was evaporated relatively rapidly (2 hr) *in vacuo* to give an orange-coloured crystalline solid. (Found: Ru, 30·3, RuNO, 38·4, N, 16·7, NO_2, 40·4, NO_3, nil, H_2O (by difference), 21·2. Calc. for $[RuNO(NO_2)_2(H_2O)_2]\ 2H_2O$, mol. wt. 341·8; Ru, 29·8, RuNO, 38·5, N, 16·4, NO_2, 40·4, H_2O, 21·1%).

Properties

A molecular weight of 140 was obtained by the depression of the freezing point of 10 g of water by 0·0814 g of this solid.

Owing to its extremely hygroscopic nature a satisfactory infra-red spectrum was not obtained.

The material behaves as a single species in 3 M $HClO_4$, because the paper chromatography of a solution (~2×10^{-2} M in Ru) showed a single broad peak (Fig. 3) with $R_F \sim 0{\cdot}5$. After standing for 18 hr the chromatogram remained unchanged.

There is reason to suppose that in water there is decomposition to the dinitro complex, since

(a) paper chromatography showed a rapid (~5 min) growth of a new peak at the solvent front; and

(b) in the same time, one mole of nitrous acid was liberated per mole of dissolved ruthenium complex.

This suggests that, unlike the di- and tetranitro complexes, this compound is not a simple nitro complex of (RuNO). Of necessity, one of the NO_2 groups is in an unsymmetrical position, which might lead to instability; also the presence of nitrito or of bridged nitro groups may account for the rapid decomposition in water.

[9] F. S. Martin, J. M. Fletcher, P. G. M. Brown and B. M. Gatehouse, *J. Chem. Soc.* 76 (1959).

COMPLEXES FORMED IN SOLUTION BY THE ACTION OF OXIDES OF NITROGEN ON (RuNO) NITRATO COMPLEXES

Evaporation during preparation of solids I and II is likely, through ligand substitution, to cause shifts in the equilibria between the various nitro-nitrato (RuNO) complexes which can exist in 3 M HNO_3. Chromatograms of solutions prior to evaporation are given in Figs. 4 and 5, and Table 4 suggests a correlation between some of the peaks obtained and the solids isolated.

The treatment given in Table 4A, which is carried out in a closed vessel, produces

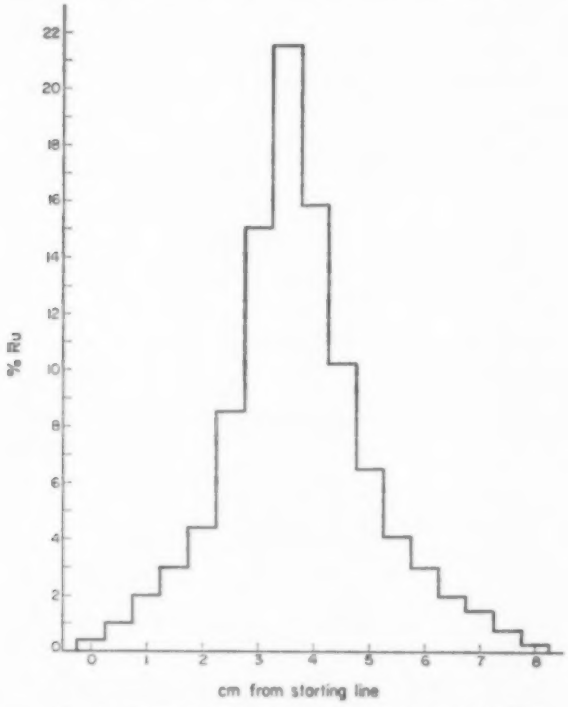

FIG. 3.—Paper chromatogram of complex II in 3 M $HClO_4$.

a distribution of complexes (Fig. 4B) which is not substantially altered by further heating in the presence of $NaNO_2$ at 50°C, and remains the same for several months. The proportions and rates of formation of the complexes are independent of the ruthenium concentration over the range 10^{-4}–10^{-1} M. Some form of mononitro complex is suggested for the material (Complex III) with $R_F \sim 0{\cdot}1$ (Fig. 4B), since a species with this R_F is not found among the (RuNO) nitrato complexes (cf. Fig. 4A). After extracting the 3 M HNO_3 solution with 30% TBP/kerosene and exhaustively stripping the solvent phase with 3 M HNO_3, a final value of D_{Ru} (0·51) is obtained which agrees with K_{Ru} for the dinitro complex under similar conditions (cf. Table 2).

The treatment given in Table 4B leads, after 7 hr, to a single species, Complex IV (Fig. 5C). This is stable in 3 M HNO_3 for periods of >1 year, and its rate of formation is independent of the ruthenium concentration. Its anionic nature is shown by the formation with silver nitrate of a pale pink precipitate, insoluble in water and acid

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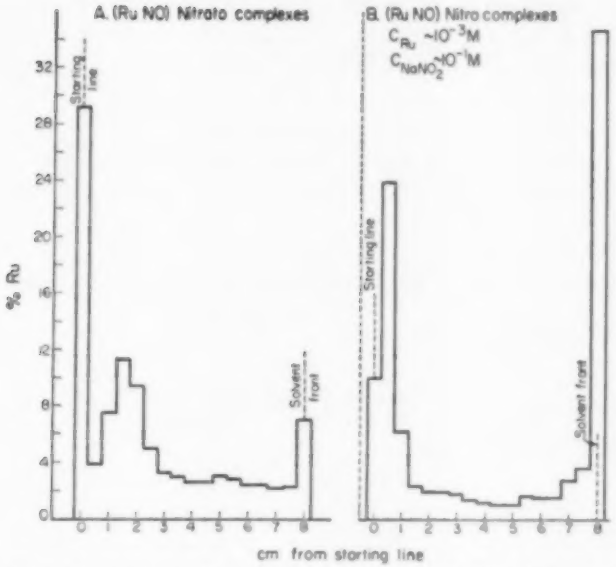

FIG. 4.—Paper chromatograms illustrating the formation of (RuNO) nitro complexes by the action of $NaNO_2$ at 50°C on (RuNO) nitrato complexes in 3 M HNO_3.

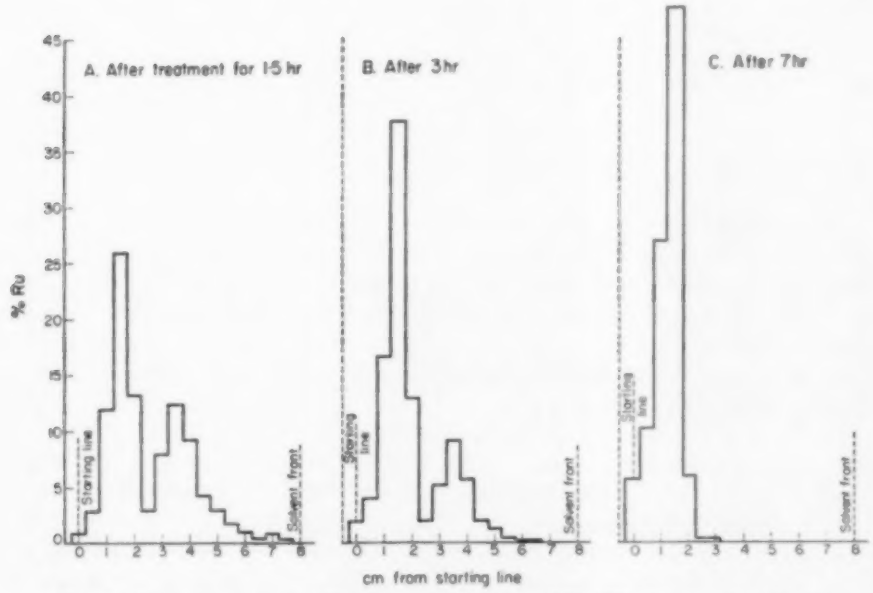

FIG. 5.—Paper chromatograms illustrating the formation of (RuNO) nitro complexes by the action of oxides of nitrogen at 65°C on (RuNO) nitrato complexes in 3 M HNO_3.

solution, which decomposes on heating. It differs from the tetranitro complex[3] in that its colour in 3 M HNO_3 is pink rather than yellow; this suggests that there is nitrito rather than nitro complexing. The complex is practically inextractable ($D_{Ru} < 10^{-4}$ from 3 M HNO_3) into 30% TBP/kerosene.

GENERAL DISCUSSION

The new nitrosylruthenium complexes that have been isolated all show the diamagnetism expected for an octahedral arrangement of $4d^2 5s 5p^3$ bonds about the Ru(II) atom.

TABLE 4.—COMPLEXES FORMED IN 3 M HNO_3 BY THE ACTION OF OXIDES OF NITROGEN ON (RuNO) NITRATO COMPLEXES

Serial	Treatment	Colour of solution (10^{-3} M Ru)	Paper chromatography peaks with R_F	Suggested correlation	
				Name	$\frac{NO_3}{Ru}$
A	$NaNO_2$ at 50°C for 1 hr	Yellow	1·0 ~0·1	Dinitro Mononitro Complex III	2 1
B	NO + NO_2 at 65°C (i) for 1–3 hr	Yellow	~0·5 ~0·2	Complex II Complex IV	3 >3
	(ii) for 7 hr	Pink	~0·2	Complex IV	>3
C	cf. sodium tetranitro complex in water	Yellow	0	Tetranitro	4

As would be expected, slow reactions ($t_{1/2} \sim$ 1–30 days at 20°C) characterise substitutions involving the nitro ligand on (RuNO)(III). In contrast, reactions involving the nitrato ligand occur with $t_{1/2}$ in the range 10–60 min at 20°C. Once formed, however, the (RuNO) nitro complexes show greater stability than their nitrato analogues, e.g.

(i) unlike the nitrato complexes, solutions of the nitro complexes are not oxidized to RuO_4 by Ce(IV), and

(ii) while the nitrato complexes are readily co-precipitated from solution with iron and calcium phosphates at pH 11·5 and with iron and calcium sulphides at pH 5·5, the nitro complexes remain largely in solution under these conditions.

It is known that pentammino cobalt(III) chloride shows structural isomerism between the nitro and nitrito forms and that, both in the solid state and particularly in acid solution, the nitro complex is the more stable.[7] Analogous complexes can be envisaged for (RuNO)(III) and the presence of a nitrito group may account for the observed instability of the preparation II with RuNO : NO_2 = 1 : 3. The yellow colour and general stability of most of these complexes suggest that they are mainly in the nitro form.

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These studies have confirmed that in nitric acid solution there can exist a range of (RuNO) complexes extending from the nitrato, through mixed nitro-nitrato to the nitro complexes. Evaporation of such solutions clearly leads, in most cases, to mixtures of complexes, and only in certain precisely controlled conditions are single species obtained.

Acknowledgements—The author wishes to thank Dr. J. M. FLETCHER for many helpful discussions. The infra-red spectra were kindly measured by Dr. B. M. GATEHOUSE at University College, London.

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COMPLEX FORMATION BETWEEN α-HYDROXY ORGANIC ACIDS AND MOLYBDIC AND TUNGSTIC ACID PREPARED BY ION EXCHANGE

E. RICHARDSON
Dept. of Chemistry, Whitehaven College of Further Education, Whitehaven, Cumberland

(*Received* 15 *June* 1959)

Abstract—Complex formation is reported between α-hydroxy carboxylic acids and tungstic and molybdic acid prepared by ion exchange. Similar carboxylic acids without hydroxyl groups do not complex. Some properties of these complexes are described.

IN an earlier paper[1] complex formation is reported between polyhydroxy compounds and molybdic acid at various pH values. Complex formation between some α-hydroxy acids and molybdic and other inorganic acids has been reported by other workers[2,3,4] using a variety of techniques. In most cases the optimum conditions for complex formation occurred at pH values greater than seven indicating that the anion of the organic acid was the effective complexing agent. In this paper, complex formation has been investigated between α-hydroxy acids and pure unbuffered molybdic and tungstic acid prepared by ion exchange, using potentiometric and conductometric techniques. Ionization of the organic acids is inhibited in the presence of the latter acids prepared by ion exchange at the concentrations employed (~0·05 M) since the pH of their solution is less than two.

Comparatively little work has been reported on the organic complexes of tungstic acid and tungstate ions and evidence for such complexes has generally been derived by indirect methods.[3,5] This is in part due to the low solubility and the instability of tungstic acid in aqueous solution. By using the ion exchange technique, tungstic acid in relatively concentrated solution (0·1 M) may easily be prepared and this acid is sufficiently stable to allow preparation of the organic complexes.

EXPERIMENTAL

Zeo Karb 225, a sulphonated polystyrene resin in the hydrogen form, was used in all studies. This resin was activated before use by alternate washings with 2 N NaOH, water, and 2 N HCl. Excess acid was removed from the column after the final regeneration by washing with distilled water until the conductivity of the washings collected was less than 3 μmhos.

Analar sodium tungstate dihydrate, $Na_2WO_42H_2O$ and Analar sodium molybdate dihydrate, $Na_2MoO_42H_2O$, were used to prepare the free acids. Both salts are sufficiently soluble in water to prepare 0·1 M solutions. The molybdic acid obtained from the column is quite stable and may be stored, then diluted to the required concentration before use. Tungstic acid is unstable and must be prepared immediately before use.

All conductance measurements were made using a Mullard Conductivity Bridge operating in the most sensitive range, with a dip type cell of constant 1·54. All pH measurements were made using

[1] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 273 (1959).
[2] E. RIMBACH and P. LEY, *Z. Phys. Chem.* **100**, 393 (1922).
[3] G. S. RAO and S. N. BANERJEE, *Proc. Natl. Acad. Sci., India* A **23**, 76 (1954).
[4] F. FAIRBROTHER and J. B. TAYLOR, *J. Chem. Soc.* 4946 (1956).
[5] D. A. LAMBIE, *Analyst* **70**, 124 (1945).

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a Cambridge pH meter with a glass calomel electrode system calibrated by buffer solutions complying with modern standards. All extinction measurements were made on a Hilger Uvispek Spectrophotometer using fused-silica cells. Appropriate blank solutions were employed. The experiments were conducted at 18°C unless otherwise specified.

The tungsten and molybdenum concentrations and ratios have been expressed throughout with respect to WO_3 or MoO_3, and were determined gravimetrically by precipitation with 8-hydroxy quinoline.

RESULTS AND DISCUSSION

1. *Complex formation between molybdic acid and α-hydroxy acids*

The effect of selected α-hydroxy acids, and similar acids without hydroxyl groups, on the conductivity of molybdic acid at various mole ratios is shown in Fig. 1. These

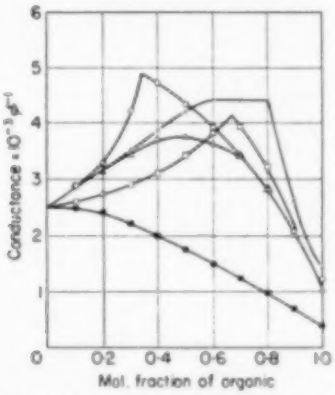

FIG. 1.—The influence of polyhydroxy acids on the conductivity of pure molybdic acid.

○ Citric acid
× Tartaric acid
△ Malic acid
□ Mandelic acid
■ Succinic and adipic acids

mole ratios were obtained by mixing the requisite quantities of 0·0425 M solutions of the two constituents. Similar curves were obtained from pH studies but since both materials were acids the effect noticed was less pronounced. Since the empirical formula of the tartaric acid complex cannot be determined from Fig. 1, a further experiment was performed for this material using various ratios of 0·085 M tartaric acid and 0·0425 M molybdic acid (Fig. 2). A sharp peak in the conductance was obtained when equal quantities of the solutions were mixed, i.e. an $MoO_3 : C_4H_6O_6$ ratio of 1 : 2. Thus from Figs. 1 and 2 it can be seen that citric, tartaric, malic and mandelic acids complex with molybdic acid at mole ratios MoO_3 : organic of 2 : 1, 1 : 2, 1 : 1 and 1 : 2 respectively, to form acids of greater strength than either constituent. Succinic acid and adipic acid, non hydroxy acids, which are included in Fig. (1) for comparison, show no tendency to complex with molybdic acid. It seems reasonable to suppose, therefore, that the complexing power of the non-ionized α-hydroxy acids and mandelic acid is due to the presence of the hydroxyl group.

The complexes are colourless in solution and show most of the normal reactions of molybdates. They give an immediate precipitate of molybdenum sulphide with hydrogen sulphide even in the absence of mineral acid, but give a coloration with

ammonium thiocyanate only after addition of HCl. A brown precipitate is obtained from all solutions on addition of potassium ferrocyanide.

Complex formation between hydroxy acids, in particular tartaric, and molybdic acid sol prepared by dialysis has been studied by BISWAS.[6,7] Optical rotation studies of the molybdotartaric acid complex in the presence of added acids showed that the tendency to complex lay in the order

$$\text{oxalic} > \text{tartaric} > \text{citric} > \text{malic}.$$

In a later study BISWAS[7] obtained a peak in conductivity and hydrogen ion concentration when tartaric acid and molybdate were present in equimolecular quantities.

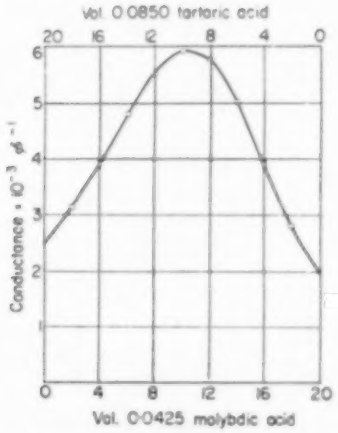

FIG. 2.—The influence of tartaric acid on the conductivity of pure molybdic acid.

It is of interest to note that, in the present study using molybdic acid prepared by ion exchange, at a lower pH value (<2), where complex formation must involve the non ionized form of the organic acid, citric acid forms a 1 : 2 complex (Org. $2MoO_3$) with molybdic acid which has a greater conductivity than the 2 : 1 (2 Org. MoO_3) complex formed by tartaric acid.

It has been shown in a previous study[8] that molybdic acid prepared by ion exchange, at the concentration used in the present study, is probably present in its simplest form as $H_2Mo_4O_{13}$. Providing degradation of the molybdic acid does not occur during complex formation, it seems possible that the greater complexing power of the citric acid may be due to a more favourable configuration of the molecule for co-ordination to a large molybdic acid molecule. Degradation of molybdic acid to simpler units may occur, however, during the formation of the organo-complexes.

Some evidence for this latter process has been obtained from a study of the ultra-violet absorption spectra both for the molybdic acid complexes and the tungstic acid complexes, which will be described later. The evidence is more conclusive in the case of the tungstic acid complexes and for convenience will be described here.

The spectra of sodium tungstate (0·005 M) acidified with perchloric acid (which

[6] A. B. BISWAS, *J. Indian Chem. Soc.* **23**, 249 (1946).
[7] A. B. BISWAS, *J. Indian Chem. Soc.* **24**, 345 (1947).
[8] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 267 (1959).

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does not complex with tungstic acid) to form solutions at various pH values is shown in Fig. 3. From this figure it can be seen that decrease in pH of the tungstate solution causes a shift of the absorption edge from the ultra-violet towards the visible region of the spectrum. A similar shift has been found for acidified molybdate solutions by many authors,[9,10] and is believed to be due to an increase in the degree of aggregation of the isopoly acid. Acidification of sodium tungstate by tartaric acid, a typical hydroxy-acid, which does not absorb appreciably in this region of the spectrum,

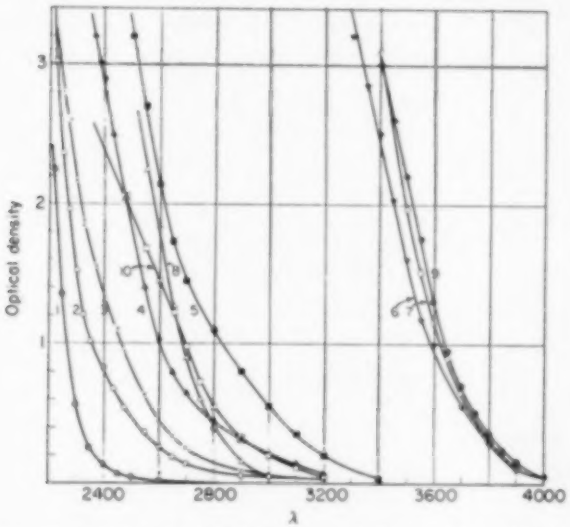

FIG. 3.—Absorption spectra of acidified tungstate solutions and tungstic acid prepared by ion exchange.

	Na_2WO_4	$HClO_4$	pH	Symbol
1	0·005 M	0	6·8	⊗
2	0·005 M	0·00042 M	6·7	○
3	0·005 M	0·00083 M	6·68	×
4	0·005 M	0·00166 M	6·55	▲
5	0·005 M	0·00332 M	6·35	■
6	0·005 M	0·0083 M	3·55	▼
7	0·005 M	0·0415 M	1·60	◇
8	0·005 M	0·05(Tartaric)	2·50	△
9	0·005 M Tungstic acid ppd. by ion exchange pH 2·7 ●			
10	0·005M Tungstic acid ppd. by ion exchange containing 0·05 M tartaric acid □			

All 1 cm cell except 10 where 0·5 cm cell used.

caused a much smaller shift. Tungstic acid freshly prepared by ion exchange has an absorption edge in the region of 3600 Å similar to acidified sodium tungstate solutions of pH $< 3{\cdot}5$. Addition of an excess of tartaric acid to ion-exchange tungstic acid to form a solution of the same tungsten content caused a shift of the absorption edge to 2700 Å. Similar results were obtained with citric acid. It seems reasonable to suppose, therefore, that some depolymerisation of the tungstic acid occurs during complex

[9] I. LINDQVIST, *Acta. Chem. Scand.* **5**, 568 (1951).
[10] P. CANNON, *J. Inorg. Nucl. Chem.* **9**, 252 (1959).

formation with the organic acids. Similar results have been obtained using tartaric acid and molybdic acid prepared by ion exchange.

2. *Complex formation between tungstic acid and α-hydroxy acids.*

The effect of selected α-hydroxy acids and similar acids without hydroxyl groups on the conductivity of tungstic acid at various mole ratios is shown in Figs. (4) and (5). In Fig. (4) the conductivity of the tartaric acid, tungstic acid mixture has been plotted after various times. Data obtained on the tungstic acid complexes are more

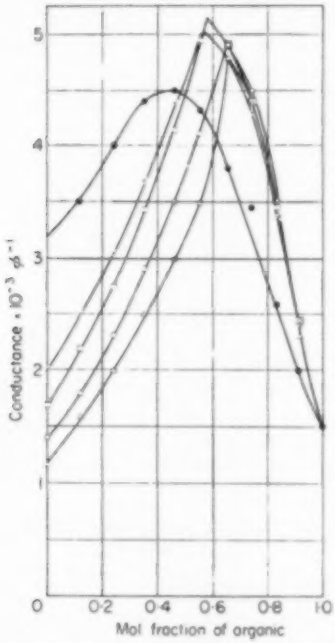

FIG. 4.—The effect of time on the conductivity of tartaric acid-tungstic acid mixtures.

● 1 hr
× 1 day
□ 2 days
○ 6 days
△ 13 days

difficult to interpret than those obtained from molybdic acid complexes. Molybdic acid is stable for several weeks but an aggregation process, causing opalescence, occurs in tungstic acid solution before preparation of the organic mixture can be completed.[11] The aggregated material probably combines much more slowly with the organic acid. The maximum conductivity is not obtained until several days after preparation even in solutions containing a stoicheiometric excess of tartaric acid, which become clear to the naked eye soon after mixing. This effect has been noted for all of the other hydroxy-acids studied and is quite reproducible under given conditions, although the time required for maximum conductivity varies for the different organic acids.

[11] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **12**, 79 (1959).

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Interpretation of the data on the tungstic acid complexes is further complicated by the slow aggregation of the tungstic acid present in stoicheiometric excess. It appears from Fig. (4), and from data for the other acids not presented, that the presence of hydroxy-organic acids decreases the rate of the aggregation process. The conductivity of several tungstic acid–organic acid mixtures at various mole ratios after standing for six days has been plotted in Fig. 5. From this figure it can be seen that tungstic acid forms complexes with gluconic, mandelic, malic, tartaric, and citric acid at WO_3 : organic acid ratios of 1 : 2, 1 : 3, 1 : 3, 1 : 2 and 1 : 1 respectively. Similar plots

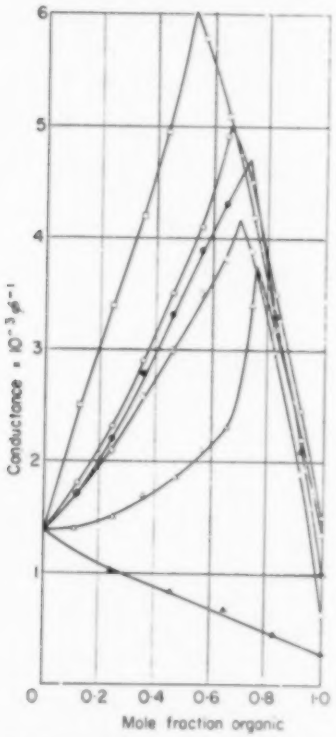

FIG. 5.—The effect of polyhydroxy acids on the conductivity of tungstic acid prepared by ion exchange.

◇ Gluconic acid
● Mandelic acid
△ Malic acid
○ Tartaric acid
□ Citric acid
▲ Adipic, Succinic } essentially the same.

after thirteen days produced peaks at the same ratios. After ten weeks peaks were still found at the same ratios except for citric acid where a 1 : 2 ratio was indicated.

In view of the time required for maximum conductivity even in solutions containing an excess of organic acid, and the possibility of decomposition of an unstable complex before six days, the existence of complexes containing a higher proportion of tungstic acid than above is not precluded. Such complexes with WO_4^{2-}/organic

ratios of 1 : 1 have been demonstrated by RAO[3] by conductometric and pH studies on sodium tungstate acidified with the organic acid. These complexes were found to be unstable immediately after preparation. The citric acid complex described by RAO,[3] however, did not have the enhanced conductivity found in the present study.

Comparison of Fig. (4) with Fig. (1) again shows that citric acid, in solutions of low pH, has the greatest complexing ability. Since adipic and succinic do not complex with tungstic acid it appears that the complex formation is again due to the presence of the hydroxyl group.

Evaporation to dryness of a sample from each solution containing the tungstate complex together with a small excess of organic acid yielded colourless crystalline products for tartaric acid and mandelic acid. Some decomposition of the citric acid and malic acid complexes occurred, however, on evaporation, giving a mixture containing yellow tungstic acid.

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SPECTROPHOTOMETRIC STUDY OF OSMIUM–1,2,3-BENZOTRIAZOLE COMPLEXES*

R. F. WILSON and L. J. BAYE
Department of Chemistry, Texas Southern University, Houston 4, Texas

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Abstract—Spectrophotometric measurements have been used to study the coloured products formed in the interaction of 1,2,3-benzotriazole with osmium. Absorbance measurements by the mole ratio method gave definite evidence of two to one and four to one 1,2,3-benzotriazole to osmium interaction products. Solutions of the lower ratio and of the higher ratio complexes were coloured green and red, respectively.

THE interaction of the osmium with 1,2,3-benzotriazole has been reported in previous papers.[1,2] In this study the method of mole ratio has been applied, using spectrophotometric measurements, to the osmium–1,2,3-benzotriazole system in an attempt to determine the stoicheiometry of the colour-forming reaction.

EXPERIMENTAL

Apparatus and procedure. Absorbance measurements were made with a Beckman quartz spectrophotometer, model DU. All readings were taken using matched 1000 cm fused silica absorption cells; for measuring solutions of very high absorbance, silica inserts were used to give an optical path of 0·097 cm. In the mole ratio study of the osmium–1,2,3-benzotriazole system, the absorbance readings were corrected for unreacted osmium in all solutions having a 1,2,3-benzotriazole to osmium mole ratio of less than two, since both the complex and the unreacted osmium (in solutions having less than the stoicheiometric amount reagents) contributed to the colour of the solution. The contribution of unreacted osmium to the total absorbance was determined by taking absorbance readings on solutions that were prepared in the usual manner less the addition of 1,2,3-benzotriazole. The effect of pH on the solutions was not studied since preliminary studies showed that, for basic media, small changes in pH did not change significantly the absorbance of the solutions. The ionic character of the osmium–1,2,3-benzotriazole was studied using a three compartment cell similar to that described by MACNEVIN and KRIEGE.[3]

Reagents. A 0·197 millimolar stock solution of osmium was prepared from osmium tetroxide obtained from A. D. Mackay, Inc. The osmium tetroxide was dissolved in 0·1 molar sodium hydroxide and was standardized using the procedure of AYRES and WELLS.[4] A stock solution of aqueous 1,2,3-benzotriazole was prepared from recrystallized reagent, Eastman Kodak Chemical No. 2759, and was standardized according to the procedure of WILSON and WILSON.[2] All other material used in the preparation of solutions were reagent grade chemicals.

Mole ratio method. The determination of reaction stoicheiometry of complexes in solutions by the mole ratio method[5,6] has been presented previously. More recently, the mole ratio method[7,8] has been extended to studies in which a series of complexes is formed under given conditions.

* This work was supported by a grant from the Robert A. Welch Foundation.

[1] R. F. WILSON and L. J. BAYE, *J. Amer. Chem. Soc.* **80**, 2652 (1958); *J. Inorg. Nucl. Chem.* **9**, 140 (1959); *Talanta* **1**, 351 (1958).
[2] R. F. WILSON and L. E. WILSON, *Analyt. Chem.* **28**, 93 (1956).
[3] W. M. MACNEVIN and O. K. KRIEGE, *J. Amer. Chem. Soc.* **77**, 6149 (1955).
[4] G. A. AYRES and W. N. WELLS, *Analyt. Chem.* **22**, 317 (1950).
[5] A. E. HARVEY and C. L. MANNING, *J. Amer. Chem. Soc.* **72**, 4488 (1950).
[6] J. H. YOE and A. L. JONES, *Industr. Engng. Chem.* (*Analyt.*) **16**, 111 (1944).
[7] A. S. MEYER and G. H. AYRES, *J. Amer. Chem. Soc.* **77**, 2671 (1955).
[8] A. S. MEYER and G. H. AYRES, *J. Amer. Chem. Soc.* **79**, 49 (1957).

For the study of the interaction of osmium with 1,2,3-benzotriazole by the mole ratio method, solutions were prepared by adding to a series of 25 ml volumetric flasks in the following order: two millilitres of ethyl alcohol, 3 ml of 0·197 millimolar osmium stock solution, and varying amounts of 1,2,3-benzotriazole solution; the resulting solutions were diluted to volume with distilled water. The freshly prepared solutions ranged from faintly pink to red in colour, with intensities somewhat dependent upon the concentration of 1,2,3-benzotriazole and time allowed for colour development. On allowing the solutions to stand at room temperature for 60 days, the time required for full colour development of all the solutions, each solution which had a mole ratio of less than 4 : 1 of reagent to osmium changed from red or pink to green and each solution which had a mole ratio equal to or

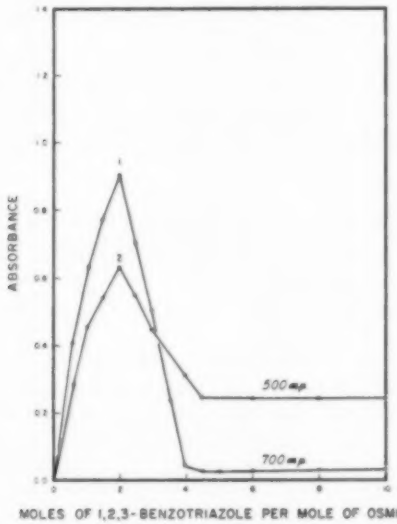

FIG. 1.—Osmium–1,2,3-benzotriazole reaction by the mole ratio method.

greater than 4 : 1 remained red in colour. These final colours of the solutions as well as their intensities, after full colour development, remained constant for at least 180 days. After full colour development the absorbancies of the solutions were measured over the wavelength region of 300–1000 mμ. Curves of Fig. 1, plots of absorbancies corrected for unreacted osmium against moles of 1,2,3-benzotriazole per mole of osmium, show well defined mole ratios of 2 : 1 and 4 : 1.

Precipitation of green complex. From the aforementioned solutions in which the mole ratio of 1,2,3-benzotriazole to osmium was 2 : 1, the green coloured complex was precipitated quantitatively by acidifying the solution with dilute nitric acid. The precipitate was filtered, washed and dried over magnesium perchlorate. (Found: Os, 39·63; C, 29·98; N, 17·69; H, 2·58. Calc. Os, 39·67; C, 30·07; N, 17·53; H, 2·73%.) The data corresponds to the formula $Os(OH)_2(C_6H_4N_2NH)_2$. Similar precipitation studies on the red coloured solutions in which the 1,2,3-benzotriazole to osmium ratio is 4 : 1 or greater have been reported previously.[1]

DISCUSSION

The spectral curves shown in Fig. 2, plots of log absorbancies against wavelengths for the 1 : 1, 2 : 1, 3 : 1 and 4 : 1 mole ratio solutions, are not superimposable at all wavelengths by translation along the log absorbance axis; therefore, the solutions do not contain identical kinds of absorbing materials.[9] In Fig. 1, the mole ratio curves show definite evidence that 2 : 1 and 4 : 1 interaction products are produced in the reaction. As the mole ratio of 1,2,3-benzotriazole to osmium was varied from

[9] M. G. MELLON (Editor), *Analytical Absorption Spectroscopy* pp. 307–310. John Wiley, New York (1950).

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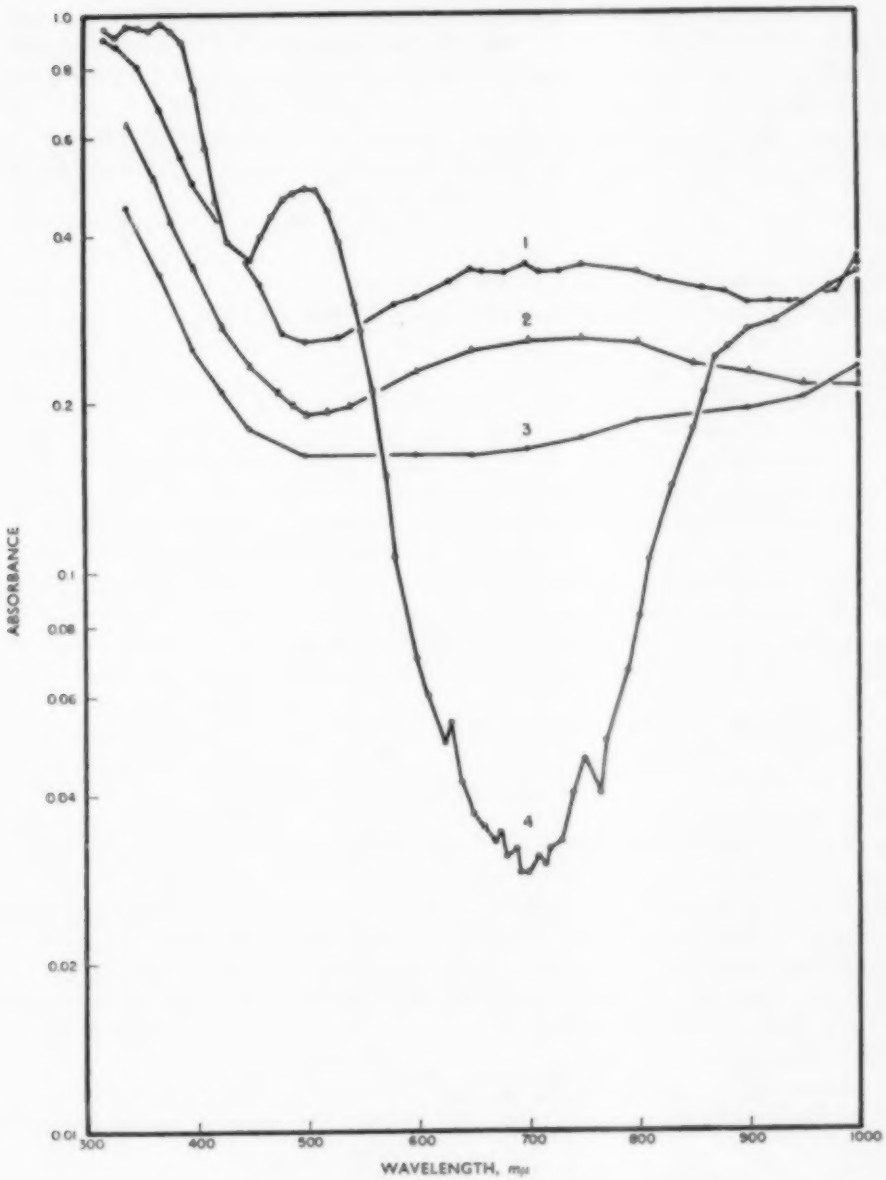

FIG. 2.—Spectral curves of solutions containing different mole ratios of 1,2,3-benzotriazole to osmium.

Curve	Conc. of Os, m molar × 100	Ratio of reagent to Os
1	8·31	2 : 1
2	8·31	1 : 1
3	8·31	3 : 1
4	40·0	4 : 1

1 : 4 to 10 : 1, absorbance measurements indicated that reaction products lower than 1 : 1 or higher than 4 : 1 are not formed. It was observed that the green coloured complex could be prepared readily from the red coloured complex by heating the red coloured complex with an excess of the stock osmium solution to which a small volume of ethyl alcohol had been added. It was further observed that the red coloured complexes could not be prepared similarly by heating the green coloured complexes with excess 1,2,3-benzotriazole. These observations suggest strongly that the red complex is favoured kinetically whereas the green complex is favoured thermodynamically. The fact that freshly prepared osmium–1,2,3-benzotriazole solution, regardless of the mole ratio relation, always ranges from pink to red gives additional support that the red complex is favoured kinetically in the reaction.

The colours of the 1 : 1, 2 : 1 and 3 : 1 mole ratio solutions of 1,2,3-benzotriazole to osmium were not adsorbed strongly on either cation or anion exchange resins. The red complex, having a mole ratio of 4 : 1 of 1,2,3-benzotriazole to osmium, was absorbed on IRA-400 anion exchange resin which suggests that the red complex showed some anion behaviour. However, as expected the red complex was precipitated when passed over the cation exchange resin since the red complex is precipitated in acidic medium.[10] Additional information on the nature of the mole ratio solutions was obtained by studying the movement of species between charged electrodes. After having been diluted with an equal volume of a buffer solution which was 0·1 M in sodium acetate and in sodium hydroxide, the solutions containing the osmium–1,2,3-benzotriazole mixture were placed in the middle compartment of a three compartment cell similar to the one described by MacNevin and Kriege.[3] The anode and cathode compartments were filled with the 0·1 M sodium acetate–sodium hydroxide buffer solution. Platinum electrodes of fairly large surface area were placed in the cathode and anode compartments and d.c. current (~200 mA) up to 400 V were available. After 1 hr and at an applied voltage of 400 V, the 1 : 1, 2 : 1 and 3 : 1 mole ratio solutions of 1,2,3-benzotriazole to osmium showed no appreciable tendency to migrate selectively to either electrode. However, absorbance measurements indicated that the 4 : 1 mole ratio or red complex showed a marked tendency to migrate selectively into the anode compartment. The migration and the ion exchange studies indicated that the green coloured mole ratio solutions exhibit an appreciable amount of non-ionic character, whereas the red coloured complex showed a significant degree of anionic character. It was also observed that the red complex formed when the 1,2,3-benzotriazole to osmium ratio was equal to or greater than 4 : 1 followed rather closely the Bouguer–Beer Law.

[10] R. F. WILSON and L. J. BAYE, *Talanta* 1, 351 (1958).

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OXYGENATION AND OXIDATION OF Co^{II}-CHELATES*

V. CAGLIOTI, P. SILVESTRONI and C. FURLANI
Department of General and Inorganic Chemistry of the University of Rome, and
Department of Physical Chemistry of the University of Trieste

(*Received* 29 *June* 1959)

Abstract—Co^{II}dihistidine and Co^{II}diglycylglycine are known to bind oxygen reversibly (oxygen carriers) and to yield compounds containing the grouping $X_5Co—O_2—CoX_5$. It is now shown that the product of the irreversible oxidation does not contain peroxo groups, but corresponds to the general formulae $[Co^{III}X_4(OH)_2]^-$, $[Co^{III}X_5(OH)]$.

SOME chelates of Co^{II} known as oxygen carriers show the property of binding oxygen reversibly.[1] The mechanism of the reaction has been studied by polarographic,[2] spectrophotometric and other methods, in the case of cobaltodihistidine ($Co\phi_2$) and cobaltodiglycylglycine ($Co(GG)_2$).

FIG. 1.
A—before oxidation ($\varepsilon_{\frac{1}{2}} = -0{\cdot}196$ V)
B, *C*—successive oxidation stages ($\varepsilon_{\frac{1}{2}} = -0{\cdot}198$ V and $-0{\cdot}200$ V)
D, *E*—successive reduction stages ($\varepsilon_{\frac{1}{2}} = -0{\cdot}196$ V and $-0{\cdot}195$ V).

In the literature it is generally agreed that an intermediate product is formed when these complexes react with oxygen; this in turn changes into a stable compound of the type $R_2Co—O—O—Co\,R_2$ which has the above-mentioned property.

The complexes of Co^{II} with histidine and with glycylglycine are polarographically oxidizable in a reversible manner to $Co^{III}\phi_2^+$ and $Co^{III}(GG)_2^+$, at potentials of approximately $-0{\cdot}200$ V and $-0{\cdot}500$ V respectively. Fig. 1 shows the successive polarograms obtained from a solution of $Co\phi_2$ buffered at pH 7·3 during coulometric oxidation (at $-0{\cdot}08$ V) and reduction (at $-0{\cdot}45$ V); similar results are obtained by the Kalouseck reversel. The polarographic behaviour changes markedly when oxygen is bound by $Co\phi_2$ to form the intermediate compound, in which oxygen is

* Presented at the International Conference on Co-ordination Chemistry; London, 6–11 April 1959.

[1] J. Z. HEARON, D. BURK and R. SHADE, *J. Nat. Cancer Inst.* **9**, 337 (1949); M. CALVIN *et al.*, *J. Amer. Chem. Soc.* **68**, 2254, 2257, 2263, 2267 and 2273 (1946); see also A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds* p. 337. Prentice Hall, New York (1952).

[2] P. SILVESTRONI and G. ILLUMINATI, *Ric. Sci.* **28**, 1211 (1958); P. SILVESTRONI, *Ibid.* **29**, 301 (1959).

reversibly bound. Fig. 2 shows a series of polarograms for solutions of $Co\phi_2$ in the presence of increasing quantities of oxygen. Curve *A* corresponds to the initial solution of $Co\phi_2$ in the absence of oxygen; curves *B*, *C* and *D* refer to successive stages of oxygenation, and curve *E* was obtained after bubbling nitrogen through the solution.

In these polarograms, three waves can be observed. The first concerns the reversible process $Co^{II}\phi_2 \rightleftharpoons Co^{III}\phi_2^+ + e^-$; it may be an oxidation wave if only $Co^{II}\phi_2$ is present in the solution besides the oxygenated complex, or a reduction wave if only

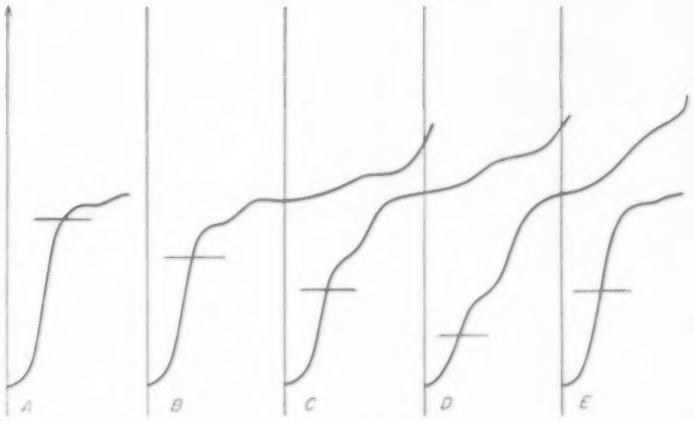

FIG. 2.
A—solution of $Co^{II}\phi_2$ in the absence of air
B, *C*, *D*—same as *A*, after passing air for 3, 6 and 9 min
E—same as *D*, after passing N_2 for 1 hr.

$Co^{III}\phi_2^+$ produced by oxidation of $Co^{II}\phi_2$ is present; if both are present, it is a redox wave. In general, soon after partial oxygenation of the solution, the first wave is almost totally an oxidation wave (curve *B*); on standing it becomes a redox wave and at later stages it becomes merely a reduction wave.

TABLE 1

Curve	i_{d_1} (1st wave) (μA)	i_{d_2} (2nd wave) (μA)	$i_{d_1} + i_{d_2}$ (μA)
A	5·10	—	5·10
B	4·40	0·68	5·08
C	3·42	1·80	5·22
D	2·25	2·95	5·20
E	5·20	—	5·20

The second wave, which increases with increasing absorption of oxygen, is produced by the addition compound. Table 1 shows that the sum of the diffusion currents of the first and second waves is constant, despite the increase in oxygenation.

The third wave is rather indefinite; its potential ($\sim -1{\cdot}0$ V) and shape, and the increase in magnitude on adding hydrogen peroxide to the solution, suggest that it

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may be attributed to the reduction of H_2O_2. The polarographic behaviour of freshly oxygenated solutions is summarized in Table 2. This behaviour may readily be correlated with the property of the complex of "carrying" oxygen. This property depends on the presence of $Co\phi_2$, and the ability of a solution of $Co\phi_2$ to bind oxygen is therefore measured by the current of the anodic portion of the first wave. The oxygen reversibly bound in such a solution is measured, at any given moment, by the diffusion current of the second wave, corresponding to the reduction of the oxygenated complex.

TABLE 2.—REDUCTION SCHEMES OF COBALTODIHISTIDINE COMPLEXES

Partially-oxygenated solutions
1st wave (−0·20 V) $Co^{II}\phi_2 \rightleftharpoons (Co^{III}\phi_2)^+ + e^-$ (redox wave)
2nd wave (−0·45 V) $(Co\phi_2)_2{\cdot}O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 + 2Co^{II}\phi_2$
3rd wave (∼ −1·0 V) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
4th wave (∼ −1·4 V) $Co^{II}\phi_2 + 2e^- \rightarrow Co^\circ + 2\phi^-$
Totally-oxygenated solutions
1st wave (−0·20 V) $(Co^{III}\phi_2)^+ + e^- \rightarrow Co^{II}\phi_2$ (reduction wave)
2nd, 3rd and 4th wave: same as above
Irreversible final product (red complex)
1st wave (−0·20 V) $(Co^{III}\phi_2)^+ + e^- \rightarrow Co^{II}\phi_2$
2nd wave (∼ −1·4 V) $Co^{II}\phi_2 + 2e^- \rightarrow Co^\circ + 2\phi^-$

The loss of the "carrying" power of the $Co\phi_2$ solution is measured by the height of the cathodic portion of the first wave, which gives the amount of Co(II) oxidized to Co(III). The final stage is irreversible; both the $Co\phi_2$ and $Co(GG)_2$ solutions contain stable red $Co^{III}X_2^+$ complexes, which are not of the type $X_2Co—O—O—CoX_2$ as may be seen from the literature. These solutions give two reduction waves; the first corresponds to the reduction of tervalent to bivalent cobalt and the second to the reduction of bivalent to zero-valent cobalt.

Further evidence of the nature of the red complex is afforded by analysis of the final product. Using the method of GILBERT *et al.*,[3] but with a slightly larger excess of H_2SO_4, we have obtained by precipitation with alcohol a microcrystalline, solid red complex with an elementary composition which corresponds satisfactorily with the formula $[Co^{III}(GG)_2OH]_2{\cdot}H_2SO_4$ or $[Co^{III}(GG)_2(H_2O)]_2^{2+}\ SO_4^{2-}$. The compound behaves as an acid of equivalent weight about 390 (calc. 386), and has an electrical conductivity of the same order as that of sulphuric acid; its apparent molecular weight, measured cryoscopically in aqueous solution, is about 170, or slightly less than one fourth of the formula weight. The infra-red spectrum of the red complex shows several strong absorption peaks at 3101, 3194, 3370 and 3570 cm^{-1} (very broad) (Table 3); since not all of these frequencies can be due to the C—H and N—H stretching of the organic ligands (the frequency at 3570 cm^{-1} is too high even for the free N—H stretching of a primary amide), the presence of an OH-grouping in the

[3] J. B. GILBERT, M. C. OTEY and V. E. PRICE, *J. Biol. Chem.* **190** 337 (1951); C. TANFORD, D. C. KIRK and M. K. CHANTOONI, *J. Amer. Chem. Soc.* **76**, 5325 (1954).

complex must be admitted. The simplest form of the final red product should then be $[Co^{III}(GG)_2OH]$ and our precipitate therefore must be its adduct with sulphuric acid. This formulation is not very different from that originally proposed by GILBERT *et al.*,[3] apart from the fact that oxygen is present not as molecular O_2 or in a peroxo bridge, but as OH^-.*

We have also measured the visible-UV absorption spectra of the initial product and of the successive stages of the reaction between the complex of Co^{2+} with glycylglycine (probably $[Co^{II}(GG)_2(OH)]^-$)[3] and oxygen (Figs. 3 and 4). The spectrum of the initial substance (Fig. 3, *A*) has exactly the same shape as those of normal complexes

TABLE 3.—PROPERTIES AND COMPOSITION OF THE RED COMPLEX (AS PRECIPITATED FROM SULPHURIC SOLUTIONS)

Analytical composition

	Found (%)	Calcd. for $[Co^{III}(GG)_2OH]_3 . H_2SO_4$ (formula-weight 772)
C	24·94	24·87
H	4·45	4·14
N	14·45	14·51
Co	14·90	15·28
SO_4^-	11·78	12·43

Ultra-violet absorption spectrum

$\nu(cm^{-1})$	$\lambda(m\mu)$	ε_M
19600	510	346
25500	392	115

Specific conductivity

Concentration (mol/l.)	λ
$4·17 \times 10^{-3}$	177
$1·83 \times 10^{-3}$	246
$1·67 \times 10^{-3}$	434

Mol. weight (cryoscopic, in water): 170 in approx. 0·1 M solutions
Equivalent weight as an acid: 390 (calcd. 386)
IR absorption peaks in the μ-region: 3101, 3194, 3370 and 3530 cm^{-1}

of bivalent Co, with one main band at 510 mμ, $\varepsilon_M \sim 5·5$; as the absorption of O_2 proceeds, a second unresolved maximum is initially formed at about 590 mμ indicating the presence of at least another intermediate in the oxidation reaction besides the brown form; in succession the brown form develops, the formula of which is probably $[Co(GG)_2]_2 \cdot O_2$, with a spectrum which exhibits an intense charge-transfer band with a maximum frequency at 29,000 cm^{-1} and $\varepsilon_M \sim 3000$.[2] (Fig. 3, *C*). This form is capable of carrying O_2 and can be reduced at the dropping mercury electrode forming successively H_2O_2 and H_2O; furthermore, it can undergo an internal redox process which gives rise to the observed charge-transfer band; the brown form is probably diamagnetic, as has been ascertained by CALVIN and

* Dr. M. T. BECK has communicated to us that he has prepared under similar conditions a bis-hydroxo-complex of the same type, with formula $NH_4^+[Co^{III}(GG)_2(OH)_2]$. (Private communication).

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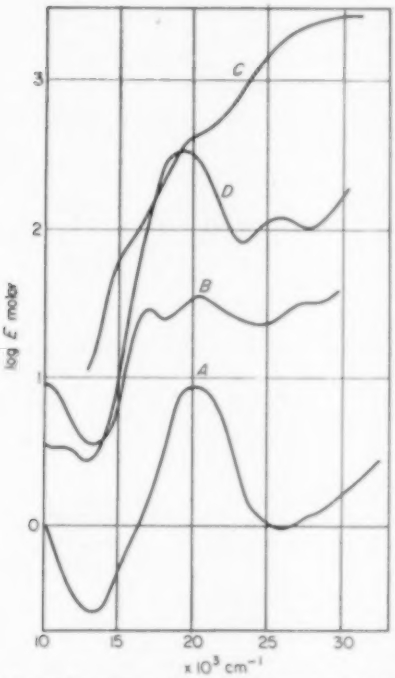
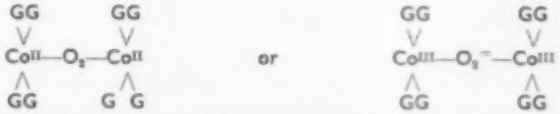


FIG. 3.—Absorption spectra of a solution containing 5×10^{-3} M Co, 0·1 M glycylglycine and 0·2 M NaOH:

A: before oxygenation
B, C, D: successive oxygenation and oxidation stages
E: after passing excess O_2 (brown form)
F: same as *E* after 1 day
G: same as *E* and *F* after two days (red form).

BARKELEW[4] for the oxygenated form of the cobaltous complexes with ligands of the salicylaldehyde-ethylenediimine type.

We are then of the opinion that this brown form is the only one which contains an O—O bridge, and its behaviour may possibly correspond to either of the two formulae:



The spectrum of the final red product (Fig. 3, *D* and Fig. 4, *G*) strongly resembles those of other octahedral or nearly-octahedral complexes of Co(III); the maxima at 520 and 390 mμ, with molar extinctions of 340 and 115 respectively, indicate a rather high ligand-field strength ($>H_2O$). It is therefore proved once again that the red form contains tervalent cobalt; we cannot however deduce solely from the spectra which ligands are bound to cobalt in this complex, but the results of all our measurements support the idea that the final red product corresponds to the formula $[Co^{III}(GG)_2(OH)]$; the irreversible reaction leading from the brown to the red form should then consist essentially in the elimination of the peroxo groups, so that the

[4] M. CALVIN and C. H. BARKELEW, *J. Amer. Chem. Soc.* **68**, 2267 (1946).

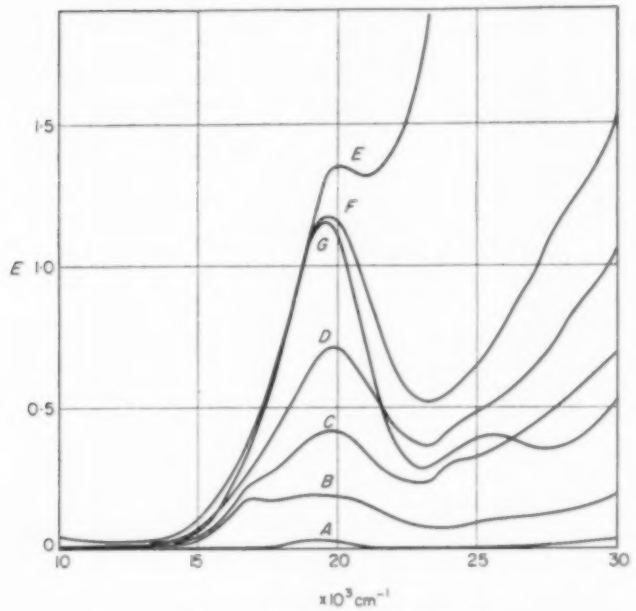


FIG. 4.—Molar absorption spectra of
A—Co^{3+} with excess glycylglycine before oxygenation
B—same as *A* in the first oxygenation stages
C—same as *A* and *B* with excess O_2 (brown form)
D—final red complex (cobalti-bis-glycylglycine hydroxide).

binuclear oxygenated complex of cobalt with glycylglycine becomes mononuclear. Since it is experimentally found that all the oxygen in the final products is reduced to water and that no more peroxo bridges are present, we must necessarily include in this stage a reaction leading to decomposition of the hydrogen peroxide, which is possibly present as an anion in the brown complex. Such a reaction could be catalysed by the cobalt ion (several metallic complexes have been reported to exhibit peroxydase activity,[5]), and occur with an oxidation of the organic part of the ligand molecules, e.g. dehydrogenation of an amino to an imino group. In this respect it should also be mentioned that HEARON and BURK[6] report the evolution of CO_2 during the reactions following the formation of oxygen-carriers from cobaltous salts, O_2, and aminoacids; quite recently BECK[7] has found that the cobaltic complex of histidine, prepared from Co^{3+} ions and histidine, has an absorption spectrum which is different from that of irreversibly-oxidized Co(II)–histidine solutions, and therefore he assumes that the organic ligand has been oxidized, as in the case with the Cu(II)–histidine complex.[8] In the case of cobalt(III) bis-glycylglycine, a metal-catalysed reaction leading to decomposition of the brown form could start with charge-transfer from the group to be oxidized to the cobalt, i.e. with the same internal process as that which probably causes the charge-transfer band observed experimentally in the spectrum of the brown form.

[5] See e.g. F. HEIN, *Chemische Koordinationslehre* Chapter H, 2, (a), (b) and (c). S. Hirzel Verlag Zuerich (1950).
[6] J. Z. HEARON and D. BURK, *Arch. Biochem.* **14**, 337 (1947).
[7] M. T. BECK, *Naturwissenschaften* **45**, 162 (1958).
[8] J. CSÀSZÀR, L. KISS and M. T. BECK, *Naturwissenschaften* **45**, 210 (1958).

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KINETIK UND MECHANISMUS DER AQUOTISIERUNG DES DIOXALATO-MONOÄTHYLEN-DIAMIN-CHROM(III)-IONS*

H. L. SCHLÄFER
Institut für physikalische Chemie, Universität Frankfurt am Main

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Zusammenfassung—Die Aquotisierung des Dioxalato-monoäthylendiamin-chrom(III)-komplexions zum Dioxalato-diaquo-ion

$$[Cr\ ox_2en]^- + 2H_2O \rightarrow [Cr\ ox_2(H_2O)_2]^- + en,$$

wobei en = Äthylendiamin und ox = Oxalat-Ion ist, wurde in wässriger perchlorsaurer Lösung (pH = 1·1–3·0) mit Hilfe von spektrophotometrischen, refraktometrischen und potentiometrischen Messungen als Dunkelreaktion untersucht. Es zeigt sich, dass die Reaktion zum $[Cr\ ox_2(H_2O)_2]^-$ in zwei Konsekutivschritten erster Ordnung abläuft. Die kinetischen Daten für den geschwindigkeitsbes immenden Schritt werden angegeben. Es wird ein Reaktionsmechanismus diskutiert.

WIR haben uns in den letzten Jahren mit der Untersuchung der Kinetik und des Mechanismus der Aquotisierung von Äthylendiaminkomplexen des III-wertigen Chroms beschäftigt. Dabei zeigte sich[1–5], dass die Substitution eines Moleküls Äthylendiamin durch zwei Moleküle Wasser in zwei Konsekutiv-Schritten erster Ordnung erfolgt. Es erschien von Interesse einen Fall zu studieren, bei dem insgesamt nur ein Molekül des Diamins substitutiert wird und das resultierende Komplexion gegen weitere Aquotisierung vollkommen resistent ist. Damit werden Komplikationen, wie sie bei der Analyse der Messdaten bei stufenweiser Aquotisierung mehrerer Aminmoleküle auftreten können, von vorne herein vermieden, und es sollte sich eine Möglichkeit bieten, genaueren Einblick in den Reaktionsmechanismus zu erhalten. Als geeignet erwies sich das $[Cr\ ox_2en]^-$-Komplexion, bei dem in wässrigen Lösungen bei pH-Werten <3 die Reaktion

$$[Cr\ ox_2en]^- + 2H_2O \rightarrow [Cr\ ox_2(H_2O)_2]^- + en \ldots \quad (1)$$
$$en + 2H^+ \rightarrow enH_2^{++}$$

quantitativ zum Diaquo-dioxalato-chrom(III)-ion verläuft, das seinerseits nicht weiteraquotisiert.

Reaktion (1) wurde mit pH–, spektrophotometrischen sowie differentialrefraktometrischen Messungen verfolgt.

A. pH-*Messungen*

Es wurden wässrige 1/100 molare Lösungen des Komplexions in $NaClO_4/HClO_4$

* Eine ausführliche Darstellung wird demnächst an anderer Stelle erscheinen: H. L. SCHLÄFER, L. MÄHLER, H. P. OPITZ u. O. KLING, *Z. Phys. Chem.* (Neue Folge) im Druck (1960).

[1] H. L. SCHLÄFER u. O. KLING, *Z. Anorg. Chem.* **287**, 296 (1956).
[2] H. L. SCHLÄFER u. H. SEIDEL, *Z. Phys. Chem.* (Neue Folge) **16**, 1 (1958).
[3] H. L. SCHLÄFER u. O. KLING, *Z. Phys. Chem.* (Neue Folge) **16**, 14 (1958).
[4] H. L. SCHLÄFER u. R. KOLLRACK, *Z. Phys. Chem.* (Neue Folge) **18**, 348 (1958).
[5] H. L. SCHLÄFER u. O. KLING, *J. Inorg. Nucl. Chem.* **8**, 320 (1958).

Standard-Lösung konstanter Ionenstärke ($\mu = 0{\cdot}16$) untersucht. Die Säurekonzentration, die vorgegeben wurde, wurde stets so gewählt, dass sie genau äquivalent dem bei der Aquotisierung freiwerdenden Äthylendiamin vorlag, das pro Molekül 2 Protonen verbraucht. In Abb. 1 sind die gefundenen Kurven der Zeitabhängigkeit des pH-Wertes für 4 verschiedene Versuchstemperaturen dargestellt. Die pH-Zeit-Kurven zeigen am Anfang eine Krümmung, die in Abb. 2 nochmals vergrössert herausgezeichnet ist. Der weitere Kurvenverlauf erscheint bei oberflächlicher Betrachtung gerade. Tatsächlich weisen die Kurven jedoch zunächst einen schwachen

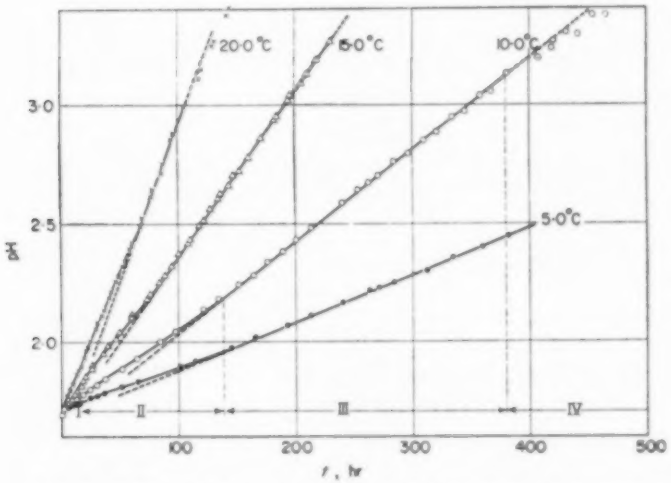

ABB. 1.—Zeitliche Änderung des pH-Wertes bei verschiedenen Temperaturen.

Durchhang auf, um dann erst bei längeren Zeiten eine Form anzunehmen, die man in guter Näherung durch eine Gerade approximieren kann. Diese Geraden sind in Abb. 1 für alle Kurven in das Gebiet geringerer Reaktionszeiten als gestrichelte Linien hineinverlängert.

Zur Interpretation der experimentellen Kurven sind folgende Möglichkeiten zu diskutieren:

(a) Einstufenreaktion erster Ordnung.

$$A \xrightarrow[2H^+]{k} C, \qquad (2)$$

wenn $A = [Cr\ ox_2en]^-$ und $C = [Cr\ ox_2(H_2O)_2]^-$ ist.

Bei der Bildung von C werden 2 Protonen verbraucht. Die Rechnung ergibt, dass in diesem Fall als pH-Zeitkurven Gerade resultieren sollten, die durch die Gleichung

$$pH = pH_0 + 0{\cdot}434k \cdot t \qquad \text{bestimmt sind.} \qquad (3)$$

(Für alle Betrachtungen gilt auf Grund der experimentellen Gegebenheiten $H_0 = 2a_0$, wenn H_0 die Protonenkonzentration zur Zeit $t = 0$ und a_0 die Konzentration von A zur Zeit $t = 0$ ist)

Da die experimentellen Kurven (vergl. Abb. 1 und 2) eine deutliche Anfangskrümmung zeigen, ist eine Einstufenreaktion erster Ordnung auszuschliessen.

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(b) Zweistufenreaktion mit zwei Konsekutivschritten erster Ordnung.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \tag{4}$$

wobei B eine Zwischenverbindung ist, über deren Natur zunächst nichts bekannt ist.

Man kann sich leicht überlegen, dass der Fall, dass im ersten Schritt 2 Protonen verbraucht werden und im zweiten keine und der umgekehrte Fall, dass im ersten Schritt keine Protonen verbraucht werden, jedoch im zweiten Schritt 2 Protonen, mit

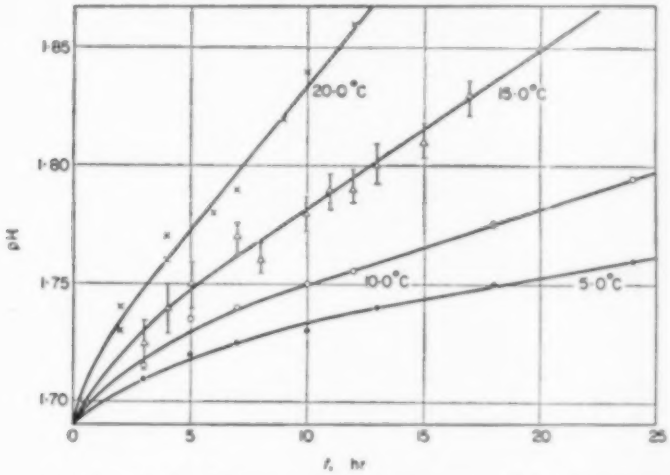

Abb. 2.—Zeitliche Änderung des pH-Wertes bei verschiedenen Temperaturen (Anfangsverlauf).

den Kurven der Abb. 1 und 2 nicht verträglich ist. Die nächste Annahme ist, dass pro Schritt ein Proton verbraucht wird

$$A \xrightarrow[H^+]{k_1} B \xrightarrow[H^+]{k_2} C. \tag{5}$$

Die Form der resultierenden pH-Zeit-Kurven, die durch die Gleichung

$$pH = pH_0 - \log\left[\left(\frac{P}{2} + 1\right)e^{-k_1 t} - \frac{P}{2}e^{-k_2 t}\right] \tag{6}$$

mit

$$P = \frac{k_1}{k_2 - k_1}$$

bestimmt sind, hängt wesentlich vom Verhältnis der Geschwindigkeitskonstanten beider Teilschritte $k_1 : k_2$ ab. In Abb. 3 sind berechnete pH-Zeitkurven für verschiedene Werte dieses Verhältnisses dargestellt, wobei für k_2 der aus dem geraden Kurventeil bestimmte Wert für die bei 15°C ablaufende Reaktion verwendet wurde. Die experimentellen Werte sind miteingezeichnet. Man erkennt, dass die experimentelle pH-Zeitkurve nur mit $k_1 > k_2$ verträglich ist. Man erhält eine Anfangskrümmung bevor die Kurven bei längeren Reaktionszeiten in einen geraden Teil übergehen. Bei geeigneter Wahl des Konstantenverhältnisses kann man zwar für den Bereich längerer Reaktionszeiten die berechnete pH-Zeitkurve mit den Messwerten zur Deckung

bringen, im Bereich der Anfangskrümmung gelingt dies jedoch nicht. Die Anfangskrümmung geht in jedem Fall später in den geraden Kurventeil über, als dies experimentell beobachtet wird.

Nimmt man an, dass im ersten Schritt n und im zweiten Schritt $2\text{-}n$ Protonen verbraucht werden, wobei $0 < n < 2$ ist, das Reaktionschema also die Form

$$A \xrightarrow[nH^+]{k_1} B \xrightarrow[(2-n)H^+]{k_2} C \tag{7}$$

besitzt, so erreicht man eine bessere Übereinstimmung der experimentellen und der berechneten pH-Zeit-Kurven, wie dies als Beispiel für die Reaktion bei 15°C in

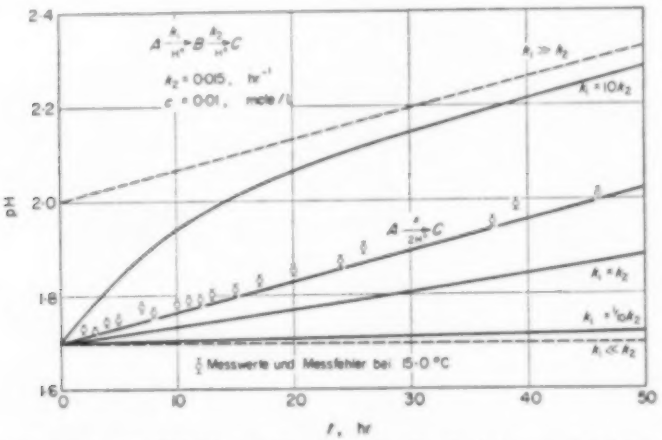

Abb. 3.—Berechnete pH-Zeitkurven für eine zweistufige Reaktion, wenn in jeder Stufe ein Proton verbraucht wird. k_1 variabel, k_2 = const.

Abb. 4 dargestellt ist. n ist der Bruchteil von B, der protoniert ist. An Stelle von Gl. (6) tritt dann die Beziehung

$$\mathrm{pH} = \mathrm{pH}_0 - \log\left[\left\{1 + P\left(1 - \frac{n}{2}\right)\right\} e^{-k_1 t} - P\left(1 - \frac{n}{2}\right) e^{-k_2 t}\right]. \tag{8}$$

Man erkennt aus Abb. 4, dass die experimentelle Kurve mit $k_1 \sim 30$–$80\ k_2$ und $n \sim 0{\cdot}15$–$0{\cdot}20$ beschrieben werden kann. Das bedeutet, dass die Zwischenverbindung B in Schema (7) nur partiell protonisiert ist. Die erste Reaktion A → B, die sehr schnell verläuft, müsste nach ca. 10 hr praktisch abgelaufen sein, sodass dann die zweite Reaktion B → C alleine geschwindigkeitsbestimmend ist. Nach einer Anfangskrümmung geht daher die pH-Zeit-Kurve in eine Gerade über.

Die Messungen zeigen jedoch—wie aus Abb. 1 zu sehen ist—, dass die pH-Zeit-Kurven keineswegs nach der Anfangskrümmung sofort in Gerade übergehen, sondern dass sie zunächst einen schwachen Durchhang aufweisen und erst bei längeren Reaktionszeiten einen geraden Verlauf annehmen.

Dies-kann man verstehen, wenn man nicht mit einem über die gesamte Reaktionszeit konstanten n-Wert rechnet, sondern einen mit der Zeit und damit mit dem pH-Wert variablen n-Wert annimmt. Das bedeutet, dass kein konstantes Verhältnis von protonierter zu nichtprotonierter Form des Zwischenkörpers B vorliegt, vielmehr

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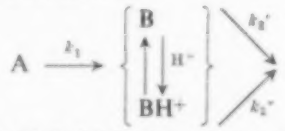
ist es naheliegend, ein pH-abhängiges Säure-Basen-Gleichgewicht anzunehmen, sodass das Reaktionsschema (7) die Form



(9)

besitzt, wobei gleichzeitig berücksichtigt ist, dass das Säure-Basengleichgewicht sich

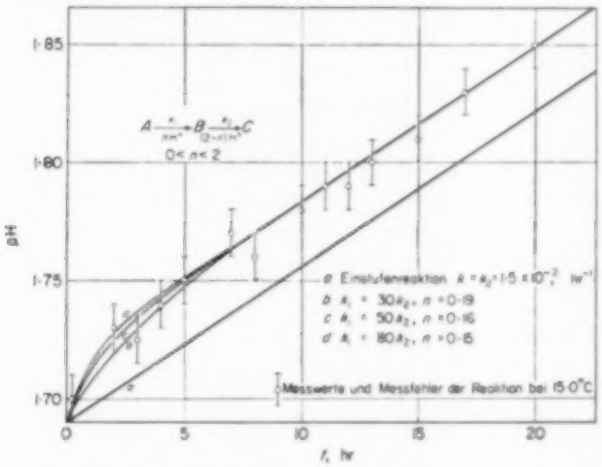


Abb. 4.—Berechnete pH-Zeitkurven für verschiedene Werte von k_1 und n (k_2 = const.).

praktisch augenblicklich einstellt. Gl. (8) nimmt dann mit $n = \dfrac{H_t}{K + H_t}$ die Gestalt

$$\mathrm{pH} = -\log\left\{-\frac{K}{2} + \frac{H_0}{4}\left[(2+P)\,e^{-k_1 t} - P\,e^{-k_2 t}\right] + \right.$$

$$\left. + \frac{1}{2}\sqrt{\left[K - \frac{H_0}{2}\left((2+P)\,e^{-k_1 t} - P\,e^{-k_2 t}\right)\right]^2 + 4\,H_0 K\left[(1+P)\,e^{-k_1 t} - P\,e^{-k_2 t}\right]}\right\} \text{ an,} \tag{10}$$

wenn $K = \dfrac{[\mathrm{B}] \cdot H_t}{[\mathrm{BH}^+]}$ die Dissoziationskonstante von BH^- (H_t = Protonenkonzentration zur Zeit t) ist und die vereinfachende Annahme gemacht wird, dass die protonierte und die nichtprotonierte Form der Zwischenverbindung praktisch gleich schnell zu C abreagieren ($k_2' \approx k_2'' = k_2$).

In Abb. 5 ist als Beispiel eine nach (10) für die bei 20°C ablaufende Reaktion berechnete pH-Zeitkurve dargestellt. Man sieht, dass die Kurve nach der Anfangskrümmung den beobachteten schwachen Durchhang aufweist, bevor sie in einen geraden Teil übergeht.

Aus dem geraden Teil der experimentellen Kurven erhält man eine Geschwindigkeitskonstante k_2, die der Reaktion vom Säure-Basen-Gleichgewicht zum Diaquo-Ion entspricht. Aus den für verschiedene Temperaturen bestimmten Geschwindigkeitskonstanten findet man eine Aktivierungsenergie von $E = 19{\cdot}8 \pm 1\%$ kcal mol^{-1}.

Die Aktionskonstante PZ beträgt $5{\cdot}0 \times 10^9 \pm 6\%$ sec^{-1}, die Aktivierungsentropie $\Delta S^* = 14{\cdot}5 \pm 12\%$ Cl mol^{-1}. Für die Dissoziationskonstante K des Säure-Basengleichgewichtes kann man einen Wert von ~ 5–8×10^{-2} abschätzen.

B. *Spektrophotometrische Messungen*

Die spektrophotometrischen Messungen wurden mit 1/100 molaren Lösungen des Komplexions in $NaClO_4/HClO_4$ Standardlösung bei gleicher Ionenstärke wie die potentiometrischen Messungen durchgeführt. Der pH-Wert wurde während der

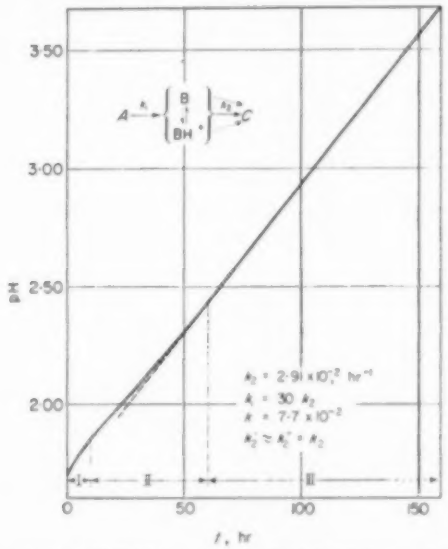


ABB. 5.—Berechnete pH-Zeitkurven unter Berücksichtigung des Gleichgewichtes $B + H^+ \rightleftarrows BH^+$ (20·0°C).

Reaktionszeit konstant auf pH $\sim$ 1·1 gehalten. Man beobachtet, wie dies in Abb. 6 für ein Beispiel (10·0°C) dargestellt ist, im Laufe der Zeit ein Absinken der Extinktion. Das Spektrum ändert sich zum Spektrum des *cis*- Diaquo-dioxalatochrom(III)-ions hin. Das resultierende Endspektrum entspricht allerdings nicht genau demjenigen des *cis*-$[Cr\ ox_2(H_2O)_2]^-$, es weist vielmehr eine etwas geringere Extinktion auf. Man beobachtet keine isosbestischen Punkte, wie dies für eine Einstufenreaktion mit nur zwei absorbierenden Gebilden zu erwarten ist[6]. Besonders im Bereich bei 450 mμ erkennt man, dass die verschiedenen Absorptionskurven keineswegs einen gemeinsamen Schnittpunkt besitzen. Daraus folgt schon, dass es sich nicht um eine Einstufen-Reaktion handeln kann.

Bei den vier durch senkrechte Pfeile gekennzeichneten Wellenlängen wurde die Zeitabhängigkeit der Extinktion für vier verschiedene Temperaturen quantitativ gemessen. Ausserdem wurden noch Vesurche mit Konzentrationen von 0·0025 M durchgeführt, deren Vergleich mit den bei Konzentrationen von 0·01 M vorgenommenen Versuchen beweist, dass nur Reaktionsschritte erster Ordnung auftreten.

Trägt man $\log (E_t - E_\infty)$ (E_t = Extinktion zu einem Zeitpunkt t, E_∞ = Extinktion nach Ablauf der Reaktion) gegen die Zeit auf, so erhält man Kurven, die zunächst

[6] H. L. SCHLÄFER u. O. KLING, *Angew. Chem.* **68**, 667 (1956).

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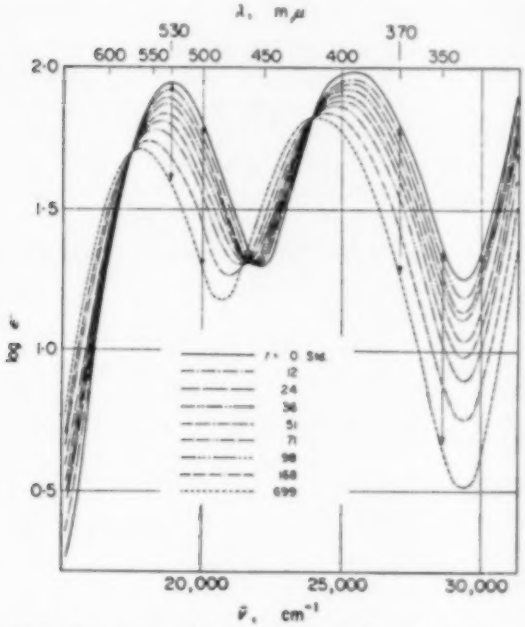

Abb. 6.—Zeitliche Veränderung des Spektrums von $[Cr\ ox_2en]^-$ in wässriger, perchlorsaurer Lösung (Dunkelreaktion). Reaktionstemperatur 10·0°C; pH ≈ 1·05; $\mu = 0{\cdot}16$.

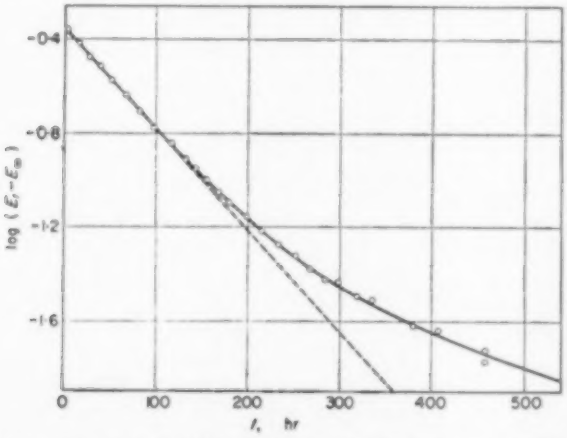

Abb. 7.—Log $(E_t - E_\infty)$ in Abhängigkeit von der Reaktionszeit. Wellenlänge 370 mμ; Reaktionstemperatur 10·0°C.

gerade verlaufen, dann aber für grössere t-Werte nach oben abbiegen. In Abb. 7 ist dies für ein Beispiel dargestellt.

Man kann dieses Verhalten verstehen, wenn man eine Reaktion mit zwei Folgeschritten erster Ordnung annimmt.

$$X \xrightarrow{k'} Y \xrightarrow{k''} Z \qquad (X = [Cr\ ox_2en]^-) \tag{11}$$

Aus Abb. 7 erkennt man, dass die Kurve $\log (E_t - E_\infty)$ für die bei 10°C verlaufende

Reaktion bis zu etwa 120 hr durch eine Gerade dargestellt werden kann. Man kann daraus schliessen, dass in diesem Bereich praktisch nur die erste Stufe X → Y wirksam ist, d.h., dass $k' \gg k''$ ist. Dann lässt sich der Schritt X → Y gesondert betrachten, und aus den Extinktionswerten des geraden Kurventeils bekommt man die Konstante k'. Aus den für verschiedene Temperaturen erhaltenen Geschwindigkeitskonstanten findet man für die Aktivierungsenergie des Schrittes X → Y $E = 19{\cdot}5 \pm 3\%$ kcal mol^{-1}, für die Aktionskonstante $PZ = 3{\cdot}4 \times 10^9 \pm 1\%$ sec^{-1} und für die Aktivierungsentropie $\Delta S^* = 14{\cdot}8 \pm 12\%$ Cl · mol^{-1}. Ein Vergleich mit den auf potentiometrischem Wege gefundenen Werten zeigt, dass es sich beim Reaktionsschritt X → Y

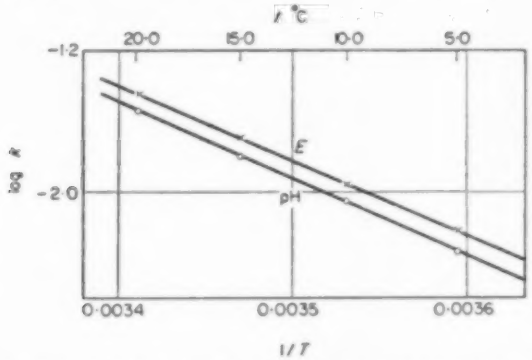

ABB. 8.—Arrhenius'sche Gerade für die RGK aus Extinktions- und pH-Messungen.

um denselben Schritt handeln muss, der auch mit Hilfe der pH-Messungen erfasst wurde, also den Schritt vom Säure-Basen-Gleichgewicht zum Endprodukt. Abb. 8 zeigt die Arrhenius'schen Geraden, die sich aus den Ergebnissen der Extinktions- und der pH-Messungen konstruieren lassen. Man erkennt, dass die mit Hilfe von spektrophotometrischen Messungen erhaltenen Konstanten um ca. 20 per cent grösser sind, als die mit Hilfe von pH-Messungen gewonnenen (vergl. Tabelle 1).

TABELLE 1.—WERTE DER REAKTIONSGESCHWINDIGKEITSKONSTANTEN AUS SPEKTROPHOTOMETRISCHEN (k_s) UND AUS pH-MESSUNGEN (k_p)

T(°C)	$k_p \times 10^2$ (hr^{-1})	$k_s \times 10^2$ (hr^{-1})	$k_p : k_s$
5·0	0·46 ± 4·8%	0·60 ± 3·3%	0·77 : 1
10·0	0·88 ± 3·1%	1·08 ± 2·8%	0·83 : 1
15·0	1·60 ± 2·5%	2·05 ± 2·0%	0·78 : 1
20·0	2·91 ± 3·6%	3·60 ± 2·2%	0·81 : 1

Die Extinktion des Zwischenkörpers Y lässt sich aus der in Abb. 7 gezeichneten gestrichelten Geraden graphisch bestimmen oder rechnerisch ermitteln. Man findet, dass Y im Rahmen der Fehlergrenze dieselbe Extinktion besitzt, wie das *cis*-$[Cr\ ox_2(H_2O)_2]^-$-Ion. Damit ist nachgewiesen, dass es sich bei Y um dieses Ion handelt.

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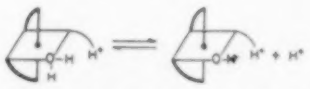
Durch Untersuchungen am System *cis*-$[Cr\ ox_2(H_2O)_2]^-$/*trans*-$[Cr\ ox_2(H_2O)_2]^-$ konnte weiterhin wahrscheinlich gemacht werden, dass der um ca. 30–50 mal langsamer ablaufende Schritt $Y \rightarrow Z$ ($k' \sim 30$–$50\ k''$) der Einstellung des *cis-trans*-Gleichgewichtes entspricht, dessen Lage pH-abhängig ist. Dieser Schritt, der mit keinem Verbrauch an Protonen verknüpft ist und somit mit den pH-Messungen nicht erfasst werden kann, bewirkt, dass infolge des dadurch gebildeten Anteils *trans*-$[Cr\ ox_2(H_2O)_2]^-$, das eine geringere Extinktion aufweist, als das *cis*-Ion, die Endextinktion etwas unterhalb derjenigen des reinen *cis*-$[Cr\ ox_2(H_2O)_2]^-$ liegt.

Der Unterschied von ca. 20 per cent zwischen den mit Hilfe von spektrophotometrischen und potentiometrischen Messungen gefundenen Reaktionsgeschwindigkeitskonstanten kann vielleicht darauf zurückgeführt werden, dass die protonierte Form des Zwischenkörpers BH^+ schneller abreagiert als die nichtprotonierte Form. Die spektrophotometrischen Messungen wurden bei konstantem pH-Wert von ~1·1 durchgeführt, die potentiometrischen bei variablen pH-Werten im pH-Intervall ~1·7–3·0. So kann man verstehen, dass die nach der pH-Methode gewonnenen Konstanten alle kleiner sind als die auf spektrophotometrischem Wege bestimmten. Nimmt man die Extinktionsmessungen ebenfalls im pH-Intervall ~1·7–3·0 vor, also unter identischen Bedingungen wie die potentiometrischen Messungen, so erhält man Werte für die Reaktionsgeschwindigkeitskonstanten, die ca. 10–15 per cent kleiner sind als die Werte, die bei pH ~1·1 gefunden wurden. Damit ist gezeigt, dass die Reaktionsgeschwindigkeit vom pH-Wert derart abhängt, dass bei höheren Wasserstoffionenkonzentrationen eine Zunahme der Reaktionsgeschwindigkeit beobachtet wird.

C. *Reaktionsmechanismus*

Die Frage nach dem Reaktionsmechanismus hängt aufs engste mit der Natur des Säure-Basengleichgewichtes $\{BH^+ \rightleftharpoons B + H^+\}$ im Schema (9) zusammen.*

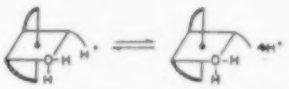
Man könnte zunächst annehmen, dass es sich dabei um ein Gleichgewicht zwischen einem Komplexion handelt, bei dem das Äthylendiaminmolekül nur mit einer NH_2-Gruppe koordiniert ist und die andere NH_2-Gruppe frei ist sowie einem Ion, bei dem diese freie Gruppe protoniert ist.



(12)

Die frei gewordene Koordinationsstelle ist durch ein H_2O-Molekül besetzt. Dem Gleichgewicht (12) würde dann eine Dissoziationskonstante von $K \sim 5$–8×10^{-2} entsprechen, die aus der Anfangskrümmung der pH-Zeitkurven nach $n = Ht/(K + H_t)$ mit $n = 0{\cdot}15$–$0{\cdot}20$ und einem mittleren pH-Wert von ~1·75, d.h. $H_t \sim 1{\cdot}78 \times 10^{-2}$ abgeschätzt wurde. Der vergleichsweise hohe Wert von K erscheint für ein Gleichgewicht vom Typ (12) sehr ungewöhnlich, wenn man bedenkt, dass die erste Dissoziationsstufe von enH_2^{++} einen pK-Wert von 6·98[7] besitzt.

Wahrscheinlicher erscheint die Annahme, dass bei den bei den Experimenten vorliegenden Wasserstoffionenkonzentrationen das freie Ende des Äthylendiaminmoleküls vollständig protoniert ist, dass jedoch das H_2O-Molekül seinen sauren Charakter zeigt.



(13)

* Für wertvolle Hinweise habe ich den Herren Dr. C. E. Schäffer und F. Woldbye (Kopenhagen) zu danken.

[7] G. Schwarzenbach, *Helv. Chim. Acta* **16**, 526 (1933).

Ein n-Wert von 0·15–0·20, der dem Protonenverbrauch pro Formelumsatz beim ersten Schritt des Schemas (7) entspricht, käme dann dadurch zustande, dass die freie NH_2-Gruppe des Äthylendiaminmoleküls 1 Proton verbraucht und durch die Dissoziation des H_2O-Moleküls Protonen (n') geliefert werden, sodass infolge $n' = 1 - n =$ 0·85–0·80 bei pH $\sim$ 1·8 etwa 80–85% der Zwischenverbindung als OH-Komplex

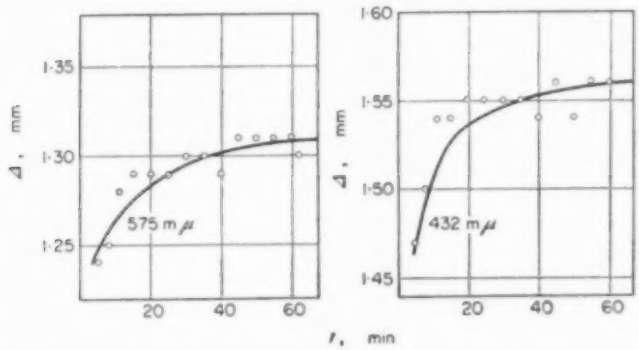


ABB. 9.—Änderung des Spaltbildabstandes Δ als Funktion der Reaktionszeit (6·0°C).

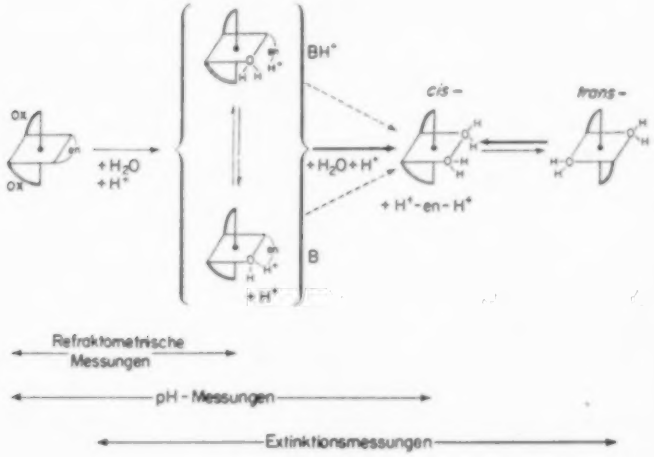


ABB. 10.—Reaktionsmechanismus.

vorliegen. Mit $n' = H_t/(K + H_t)$ erhält man für die Dissoziationskonstante des Gleichgewichtes (13) einen Wert von $2\text{–}5 \times 10^{-3}$. Auch dieser Wert erscheint verhältnismässig gross. Die pK-Werte für die Dissoziation beider H_2O-Moleküle in $[Cr\ ox_2(H_2O)_2]^-$ sind für die *cis*- $pK_1 = 7{\cdot}5$; $pK_2 = 10{\cdot}5$ und für die *trans*-Verbindung $pK_1 = 7{\cdot}5$; $pK_2 = 9{\cdot}7$ für eine Temperatur von 8°C[8]. $[Cr(H_2O)_6]^{3+}$ besitzt allerdings einen pK_1-Wert von 3·9 (15°C)[9].

[8] G. E. CUNNINGHAM, R. W. BURLEY u. M. T. FRIEND, *Nature Lond.* **169**, 1103 (1952).
[9] G. MATTOCK, *Acta Chem. Scand.* **8**, 777 (1954).

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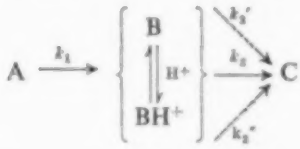
Bei der Diskussion des Säure-Basengleichgewichtes ist eventuell eine partielle Protonierung der Oxalatliganden mit zu berücksichtigen. Die erste Dissoziationskonstante von Oxalsäure hat den Wert $5{\cdot}9 \times 10^{-2}$[10]. Untersuchungen zur Klärung dieser Frage sind im Gange.

Aus der Analyse der pH-Messungen wurde das Reaktionsschema (9) abgeleitet und aus der Analyse der Extinktionsmessungen das Reaktionsschema (11). Beide Schemata sind in (14) untereinandergestellt.



(14) pH-Messungen

spektroph. Messungen.

Der zweite Schritt im ersten Schema ist mit dem ersten Schritt im zweiten Schema, wie aus dem Vergleich der kinetischen Daten folgt, identisch. Der Schritt $Y \rightarrow Z$, der mit keinem Protonenverbrauch verbunden ist, und der in einer langsamen Einstellung des *cis-trans*-Gleichgewichtes des Diaquo-ions besteht, lässt sich lediglich spektrophotometrisch erfassen. Mit den pH-Messungen wird ein schneller erster Schritt vom $[Cr\ ox_2en]^-$ zum Säure-Basengleichgewicht angezeigt, der spektrophotometrisch nicht beobachtet wird. Dieser schnelle Schritt kann aber mit Hilfe von refraktometrischen Messungen qualitativ erfasst werden. Er gibt sich, wie aus Abb. 9 ersichtlich ist, in einer schnellen Zunahme der Brechungszahl der Lösung zu Beginn der Reaktion zu erkennen. Abb. 9 zeigt die Ergebnisse differentialrefraktometrischer Messungen bei zwei Wellenlängen und der Reaktionstemperatur 6°C. Der Brechungsindex steigt innerhalb von 60 Minuten auf einen Grenzwert an; während dieser Zeit beobachtet man noch keinerlei Änderung des Absorptionsspektrums. Ein Schema für den Reaktionsmechanismus, das mit allen experimentellen Befunden in Übereinstimmung ist, ist in Abb. 10 angegeben. Eine eventuell mögliche Beteiligung des Oxalatliganden am Säure-Basen-Gleichgewicht ist dabei nicht berücksichtigt.

[10] D'ANS LAX, Taschenbuch, 2. Auflage 1943.

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 112 to 118. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF THE STABILITY CONSTANTS OF THORIUM NITRATE COMPLEXES WITH ANION-EXCHANGE RESINS

J. DANON
Centro Brasileiro de Pesquisas Físicas, Avenida Wenceslau Brás 71, Rio de Janeiro, Brasil

(*Received* 3 *June* 1959)

Abstract—The distribution of thorium between Dowex-1 nitrate resin and solution was measured by the aid of ^{234}Th in the range—1·55–8·44 M lithium nitrate. The activity of nitrate in the resin was determined and a distribution curve corrected from invasion-effects of the supporting electrolyte in the resin phase was constructed according to the Marcus and Coryell methods. The stability constants of the complex thorium species, considered to be formed from the uncharged complex

$$Th(NO_3)_4 \rightleftarrows Th(NO_3)_{4-i}^{i} + iNO_3$$

were calculated by curve fitting methods for $i = 1$ to $+2$, and the following values were found: $\log \beta_{+1} = +0{\cdot}22$, $\log \beta_0 = 0{\cdot}00$, $\log \beta_{-1} = -0{\cdot}80 \pm 0{\cdot}17$, $\log \beta_{-2} = -1{\cdot}70 \pm 0{\cdot}22$.

THE determination of the stability constants of the nitrato complexes of thorium has been investigated by solvent-extraction methods. Using a solution of thenoyltrifluoracetone in benzene as extracting agent with nitrate media of 0·5 ionic strength DAY and STOUGHTON[1] found the value 4·73 for the first nitrate complex of thorium. ZEBROSKY *et al.*[2] using the same extractant at $\mu = 5{\cdot}97$ have found the constants 2·83 for $Th(NO_3)^{3+}$ and 1·41 for $Th(NO_3)_2^{2+}$. FOMIN and MAIOROVA[3] investigated the distribution of trace amounts of thorium between an acidic nitrate solution at $\mu = 2$ and varying concentrations of tributylphosphate in benzene. These authors have found the stability constants of the complexes, $Th(NO_3)_x^{4-x}$ to be $6 \pm 0{\cdot}5$, 13 ± 1, $10 \pm 0{\cdot}5$ and $5{\cdot}5 \pm 0{\cdot}5$, for $x = 1$ to 4 respectively. Further studies[4] have shown that these values remain valid at high concentrations of thorium nitrate, suggesting that in such conditions thorium forms only mononuclear complexes with the nitrate ligand.

Some knowledge of the stability constants of the negatively charged complexes of thorium, which cannot be derived from the solvent-extraction data, appears to be of interest. Several properties of thorium in concentrated nitrate solutions, such as the formation of $M_2Th(NO_3)_6$ compounds, the extraction by oxygenated organic solvents,[5] the migration in the electric field, and the anion-exchange behaviour[6,7] are apparently influenced by the presence of complexes with negative charge.

A rigorous treatment of the sorption by anion-exchange resins of metal anion complexes from aqueous solutions has been developed recently by MARCUS and CORYELL.[8,9,10] These authors have derived a method for the evaluation of stability

[1] R. A. DAY and R. W. STOUGHTON, *J. Amer. Chem. Soc.* **72**, 5662 (1950).
[2] E. L. ZEBROSKY, H. W. ALTER and F. K. HEUMANN, *J. Amer. Chem. Soc.* **73**, 5646 (1951).
[3] V. V. FOMIN and E. P. MAIOROVA, *Zh. Neorg. Khim.* **1**, 1703 (1956).
[4] V. V. FOMIN and E. P. MAIOROVA, *Zh. Neorg. Khim.* **1**, 2749 (1956).
[5] H. IRVING, *Quart. Rev.* **5**, 200 (1951).
[6] J. DANON, *J. Amer. Chem. Soc.* **78**, 5953 (1956).
[7] J. DANON, *J. Inorg. Nucl. Chem.* **5**, 237 (1958).
[8] Y. MARCUS, *Acta Chem. Scand.* **11**, 619 (1957).
[9] M.I.T. Laboratory for Nuclear Science, Progress Report, 31 August 1957.
[10] Y. MARCUS and C. D. CORYELL, *Bull. Res. Council Israel* **8A**, 1, 17 (1959).

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constants which is particularly suitable for the species formed in the neighborhood of the neutral complex.

DISCUSSION AND RESULTS

The adsorption of thorium by Dowex-1, 8% DVB, 50–100 mesh in the nitrate form was investigated with thorium-234 (β, γ, 24·1 days period). This isotope was separated from large amounts of uranium in 8 M HCl solution with Dowex-1 columns.[11] Further purification was made by adsorbing ^{234}Th in a small Dowex-1 column from 7 M HNO_3 solution; followed by elution with water. All measurements were made in a scintillation counter.

We shall assume the following mechanism[8,9,10] for the adsorption of thorium from lithium nitrate media by the anion-exchange resin. The neutral complex $Th(NO_3)_4$ is transferred from the aqueous solution to the resin phase

$$ThL_4\ (sol.) \rightleftarrows ThL_4\ (res.) \tag{1}$$

followed by the reaction with the resin ligands

$$ThL_4\ (res.) + 4RL \rightleftarrows R_4ThL_8 \tag{2}$$

where L stands for the nitrate ligand. The number of resin ligands was chosen in order to form the coordinatively saturated complex in the resin phase. As has been shown by KATZIN *et al.*[12] the co-ordination number of Th^{4+} is in general eight.

From (1) and (2) we can write for the thermodynamic equilibrium equation of the adsorption process

$$K_r = a_{R_4ThL_8} \cdot a_{ThL_4}^{-1} \cdot a_{RL}^{-1} \tag{3}$$

or

$$K_r = [R_4ThL_8] \cdot \gamma_{R_4ThL_8} \cdot a_{ThL_4}^{-1} \cdot a_{RL}^{-1} \tag{4}$$

where brackets represent concentrations and γ the corresponding activity coefficients.

The distribution coefficient D is given by

$$D = \frac{[R_4ThL_8]}{[Th^{4+}] + [ThL^{3+}] + [ThL_2^{2+}] + \ldots} \tag{5}$$

The sum in the denominator extends to all species which can be formed in aqueous solution.

From (4) and (5) we obtain

$$D = K_r \cdot \gamma_{R_4ThL_8}^{-1} \cdot a_{RL}^{4} \cdot \frac{1}{[Th^{4+}]\, a_{ThL_4}^{-1} + [ThL^{3+}]\, a_{ThL_4}^{-1} + \ldots} \tag{6}$$

We shall now define the formation of a complex by relating it to the neutral complex

$$ThL_4 \rightleftarrows ThL_{4-i}^{i} + iL \tag{7}$$

where the index i gives the charge of the complex.

The thermodynamic equilibrium constant for (7) is

$$\beta_i = a_{ThL_{4-i}^{i}} \cdot a_L^{i} \cdot a_{ThL_4}^{-1} \tag{8}$$

[11] K. A. KRAUS, G. E. MOORE and F. NELSON, *J. Amer. Chem. Soc.* **78**, 2692 (1956).
[12] L. I. KATZIN, J. R. FERRARO, W. W. WENDLANDT and R. L. MCBETH, *J. Amer. Chem. Soc.* **78**, 5139 (1956).

which gives

$$\frac{[ThL_4^{i}{}_{-i}]}{a_{ThL_4}} = \beta_i \gamma_i^{-1} a_L^{-i}. \tag{9}$$

Introducing (9) into (6) we get

$$D = K_r \cdot \gamma_{R_4ThL_8}^{-1} \cdot a_{RL}^{4} \cdot (\Sigma \beta_i \gamma_i^{-1} a_L^{-i})^{-1} \tag{10}$$

We shall now make the following assumptions:

(1) The activity of the nitrate ion in solution is given by

$$a_L = [L] \cdot \gamma_{(LiNO_3)}^{\pm} \tag{11}$$

where [L] is the concentration of nitrate ion in the aqueous phase and $\gamma_{(LiNO_3)}^{\pm}$ the corresponding mean ionic activity coefficient of $LiNO_3$.

(2) The activity of the nitrate ion in the resin phase is given by

$$a_{RL} = a_L \cdot [L]_R^{-\frac{1}{4}} \cdot [Li]_R^{-\frac{1}{4}} \tag{12}$$

where a_L is the activity in the aqueous phase according to (11) and $[L]_R$ and $[Li]_R$ the concentrations of nitrate and lithium respectively in the resin phase. The reference state for the activity a_{RL} is taken arbitrarily as a_{RL}^{0} for $a_L = 1$.

Relation (12) can be derived from Donnan equilibrium of the electrolyte between the aqueous solution and the resin phase.[13]

(3) The activity coefficients $\gamma_{R_4ThL_8}$ and γ_i are independent of the value of a_L. The justifications for these assumptions are given in MARCUS and CORYELL papers.

Introducing the above assumptions in (10) we find

$$\log D = \log (K_r \cdot \gamma_{R_4ThL_8}^{-1} \cdot a_{RL}^{4_0}) + 4(\log a_{RL} - \log a_{RL}^{0}) - \log \Sigma \beta_i \gamma_i^{-1} a_L^{-i} \tag{13}$$

We shall now make

$$K_r^{*} = K_r \cdot \gamma_{R_4ThL_8}^{-1} \cdot a_{RL}^{4_0} \tag{14}$$

$$\beta_i^{*} = \beta_i \gamma_i^{-1} \tag{15}$$

According to the assumptions made K_r^{*} and β_i^{*} are independent of a_L.

We define a correction function $F(a)$ as

$$F(a) = \log a_{RL} - \log a_{RL}^{0} \tag{16}$$

Introducing (14), (15) and (16) into (13) we find

$$\log D = \log K_r^{*} + 4F(a) - \log \Sigma \beta_i^{*} a_L^{-i} \tag{17}$$

The difference $\log D_0 = \log D - 4F(a)$ gives the distribution coefficients corrected from the invasion effects of the supporting electrolyte in the resin phase:

$$\log D_0 = \log D - 4F(a) = \log K_r^{*} - \log \Sigma \beta_i^{*} a_L^{-i} \tag{18}$$

It is easily calculated that

$$\frac{d \log D_0}{d \log a_L} = \bar{i} = 4 - \bar{n} \tag{19}$$

where $\bar{i}$ is the mean charge number of the complex species and $\bar{n}$ the mean number of ligands as defined by Bjerrum.

[13] K. A. KRAUS and G. E. MOORE, *J. Amer. Chem. Soc.* **75**, 1457 (1953).

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The values of the distribution coefficients as a function of the $LiNO_3$ molarity are given in Table 1. This data was obtained in equilibration experiments (24 hr) with the resin at room temperature (25 ± 3°C). The concentration of the $LiNO_3$ solutions was measured in a flame photometer. All $LiNO_3$ solutions were made 0·07 M in

TABLE 1

M_{LiNO_3}	log D	M_{LiNO_3}	log D
1·55	1·10*	4·02	2·81
2·00	1·45*	4·35	2·91
2·39	1·72*	5·06	3·21
2·53	1·83	5·20	3·35
2·89	2·21	6·24	3·69*
3·40	2·36	6·32	3·67*
		8·44	4·33*

* Values with errors larger than ±0·05 log units.

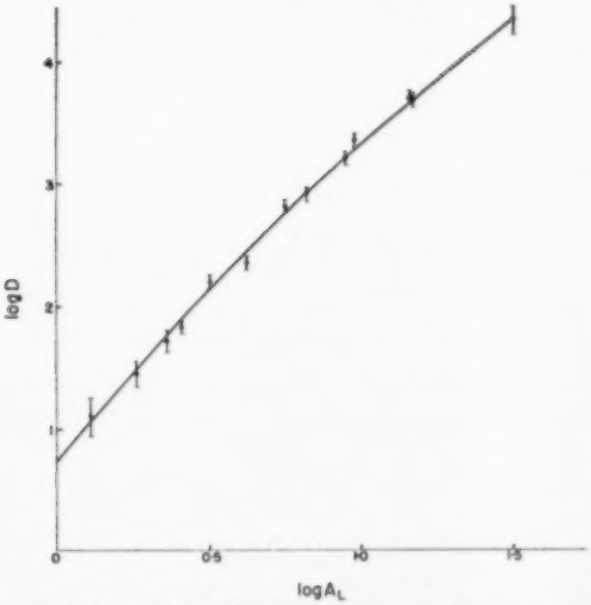

FIG. 1.—Adsorption of Th(IV) by Dowex-1 at varying $LiNO_3$ activities.

HNO_3 in order to avoid hydrolysis of thorium nitrate. However even at these acidities hydrolytical reactions appear to occur at $LiNO_3$ molarities lower than 2 M.†

Fig. 1 shows the values of log D as a function of log a_L. The values of log a_L were calculated from mean activity coefficients of $LiNO_3$ taken from ROBINSON and STOKES.[14]

† Experiments with 0·1 g of glass wool per 10 ml of solution showed in these conditions glass adsorption in amounts which are not negligible compared to the resin adsorption.

[14] R. A. ROBINSON and R. H. STOKES, *Electrolyte Solutions*. Butterworths Scientific Publications, London (1955).

Fig. 2 shows the variation of the invasion function $F(a)$ with $\log a_L$. This data was obtained with Dowex-1, X-8, 50–100 mesh in the nitrate form, from the same batch as was used in the equilibration experiments with thorium, according to the procedure described by KRAUS and NELSON.[13] Details about this data will be published in a further paper.

Fig. 3 shows the variation of the corrected distribution $\log D_0$ as a function of $\log a_L$.

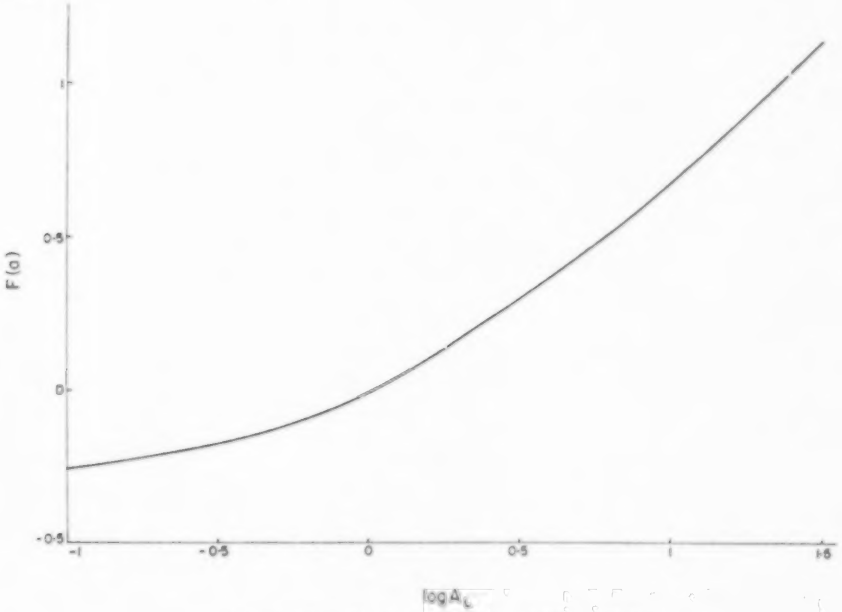

FIG. 2.—Invasion function $F(a)$ vs. $LiNO_3$ activity.

In the range of activities investigated the values of $\bar{\imath} = d \log D_0/d \log a_L$ go from $+0{\cdot}6$ to $-1{\cdot}8$ indicating the presence of the successive species ThL_3^+, ThL_4^0, ThL_5^-, ThL_6^{2-} in solution.

Preliminary values of β_{+1}^*, β_0^*, β_{-1}^* and β_{-2}^* constants were derived from the relation

$$\log \frac{\beta_i^*}{\beta_{i+1}^*} = -\log a_L \qquad (\bar{\imath} = i + \tfrac{1}{2})$$

With the values obtained for β_{+1}^* and K_r^* we formed the equation in three parameters which was solved by curve fitting method of SILLÉN:[15]

$$\frac{1}{D_0} - \frac{\beta_{+1}^*}{K \,.\, a} = \frac{1}{K} + \frac{\beta_{-1}^*}{K} \,.\, a + \frac{\beta_{-2}^*}{K} \,.\, a^2 \tag{20}$$

With the values of K_r^* and β_{-2}^* obtained from (20) we solved the equation

$$\frac{K_r^*}{D_0} \,.\, \frac{a}{\beta_{-2}^*} - a^2 = \frac{\beta_{+1}^*}{\beta_{-2}^*} + \frac{1}{\beta_{-2}^*} \,.\, a + \frac{\beta_{-1}^*}{\beta_{-2}^*} \,.\, a^2 \tag{21}$$

[15] L. G. SILLÉN, *Acta Chem. Scand.* **10**, 186 (1956).

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By this procedure the following set of values were derived for the constants: $\log K_r = 1{\cdot}22$; $\log \beta_{+1}^* = +0{\cdot}22$; $\log \beta_0 = 0{\cdot}00$; $\log \beta_{-1}^* = -0{\cdot}80 \pm 0{\cdot}17$; $\log \beta_{-2}^* = -1{\cdot}70 \pm 0{\cdot}22$.

With these values the solid curves shown in Fig. 1 and Fig. 3 were calculated from equations (17) and (18) respectively. The fitting of the experimental points is satisfactory. The data could also be fitted by a curve $\log D_0 = \log K_r^* - \log(1 + \beta_{-1}^* a + \beta_{-2}^* a^2)$ which would mean that no $Th(NO_3)_3^+$ species are present at the lower activity

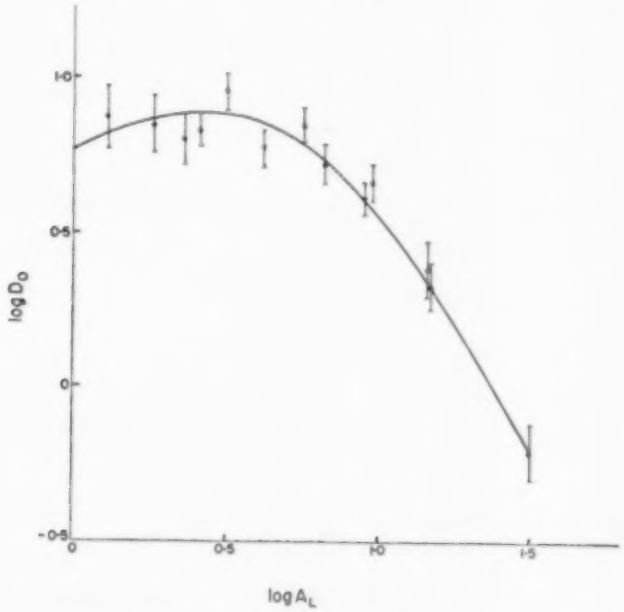

FIG. 3.—Corrected distribution vs. $LiNO_3$ activity.

range investigated. However at low $LiNO_3$ activities the hydrolytical reactions of thorium nitrate tend to increase the values of the distribution coefficients. For this reason the value found for β_{+1}^* may be considered as the upper limit of the association constant.

The comparison between the values of stability constants β_i^* (referred to the neutral complex) calculated from FOMIN and MAIOROVA's data[3] and those obtained from the anion-exchange data is shown in Table 2.

In the above comparison we disregard differences in activity coefficients between the two set of data. The stability constants β_i^* calculated from the anion-exchange data represent the product of true thermodynamic equilibrium constants by activity coefficients γ_i whereas FOMIN and MAIOROVA's data are concentration constants evaluated at constant ionic strength.

The values obtained for β_{-1}^* and β_{-2}^* show that the formation of thorium nitrate negatively charged complexes occur at high concentrations of nitrate ion (>3 M). This is in agreement with the results of FOMIN and MAIOROVA[3] which have shown that the extraction behaviour of thorium nitrate by TBP up to a concentration of 2·2 M

in nitrate ion was essentially not influenced by the formation of negatively charged complexes.

No evidence was found in the range of activities investigated for the presence of complexes with more negative charge than -2, although the possibility of the existence of such species at higher activities of nitrate ion cannot be ruled out entirely on the basis of the anion-exchange data.

TABLE 2

	$\log \beta_{+1}^{\bullet}$	$\log \beta_{0}^{\bullet}$	$\log \beta_{-1}^{\bullet}$	$\log \beta_{-2}^{\bullet}$
FOMIN and MAIOROVA ($\mu = 2$)	+0·26	0·00	—	—
Present work (variable $LiNO_3$)	+0·22	0·00	−0·80	−1·70

The overall stability constant for the reaction

$$Zr^{4+} + 6NO_3^- \rightleftarrows Zr(NO_3)_6^{2-}$$

has been investigated by solvent extraction studies with TBP[16] and its value was found to be $\beta_6 = 0{\cdot}02$, at $\mu = 4$. From FOMIN and MAIOROVA's data and the results of the present study we found for the analogous reaction for Th^{4+} the value $\beta_6 = 0{\cdot}11$. This shows an increasing tendency in the stability of the negatively charged nitrato complexes with increasing ionic radius in going from Zr^{4+} to Th^{4+}. The same trend was observed with the first nitrato complexes of these elements.[17]

Acknowledgements—We are indebted to MISS Z. CAILLAUX for the lithium analysis. This work was supported by the Conselho Nacional de Pesquisas.

[16] A. S. SOLOVKIN, *Zh. Neorg. Khim.* **2**, 611 (1957).
[17] J. C. HINDMAN, *Ionic and Molecular Species of Plutonium in Solution*, NNES, Plutonium Project Record, Vol. 14-A, p. 341. McGraw-Hill, New York (1954).

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EXTRACTION OF THE LANTHANIDES WITH ACETYLACETONE

W. B. BROWN, J. F. STEINBACH and W. F. WAGNER
Department of Chemistry, University of Kentucky, Lexington, Kentucky

(*Received* 22 *June* 1959)

Abstract—Acetylacetone extracts the lanthanides from aqueous solution at pH values between four and six. The solubility and extractability of the rare earth acetylacetonates vary with the ionic radii of the central metal ions. Extraction of the lanthanides with acetylacetone is enhanced by the decrease in basicity of the central metal ion. While separations based on differences in the pH 1/2 values of these chelates would be at best fractional, the variations in solubility and in the partition coefficients of these chelates make separations possible.

ACETYLACETONE promises to be a useful reagent for the separation of the rare earths by solvent extraction. While the lanthanide acetylacetonates are familiar compounds, a complete study of their extraction behaviour has not been undertaken. KRISHEN reported that the acetylacetonates of lanthanum and praseodymium are insoluble in acetylacetone.[1] RYDBERG found that the extraction of lanthanum and samarium acetylacetonates with benzene, chloroform, or hexone is poor.[2] However, MOELLER has reported that several of the rare earth acetylacetonates have measurable solubility in some organic solvents.[3] Moreover, SCHWEITZER and SCOTT have extracted yttrium from aqueous solutions with acetylacetone.[4] Although lanthanum, praseodymium and samarium acetylacetonates should be representative of the lanthanides in general, these investigations indicate that differences in the solubility and extractability of the rare earth acetylacetonates may exist.

MOELLER has investigated the extraction of the neodymium and erbium 5,7-dichloro-oxinates.[5] The proximity of the extraction curves for these chelates indicate that separation by solvent extraction would be impractical by this system.

DYRSSEN, among others, has studied the rare earth extraction with oxine.[6] While this system may be used to separate lanthanum from samarium, it probably would be less successful in separating the intervening rare earths.

The extraction curves for the lanthanides in the oxinate systems approach 100 per cent extraction. This may be compared with the acetylacetone system where yttrium approaches 60 per cent extraction and lanthanum and samarium have considerably lower plateaus.[3,4] This phenomenon may represent a trend in the rare earth–acetylacetone system. That is, the maximum per cent extraction and the solubility of the rare earth acetylacetonates may be functions of the ionic radii of

[1] A. KRISHEN, Doctor's Dissertation, University of Pittsburgh (1957).
[2] J. RYDBERG, *Arkiv. Kemi* **9**, 95 (1955).
[3] T. MOELLER and W. F. ULRICH, *J. Inorg. Nucl. Chem.* **2**, 164 (1956).
[4] G. K. SCHWEITZER and H. E. SCOTT, *J. Amer. Chem. Soc.* **77**, 2753 (1955).
[5] T. MOELLER and D. E. JACKSON, *Analyt. Chem.* **22**, 1393 (1950).

the rare earths. A similar trend is indicated in the rare earth–cupferron system.[6] Samarium cupferrate has a larger partition coefficient than lanthanum cupferrate.

This paper describes the extraction curves of the rare earth acetylacetonates.

EXPERIMENTAL

Apparatus and reagents

Acetylacetone, commercially available, was purified by washing with dilute ammonium hydroxide and water followed by distillation.[7] The purified product was stored over water.

The rare earth oxides were obtained in high purity from Lindsey Chemical Company and Michigan Chemical Company.

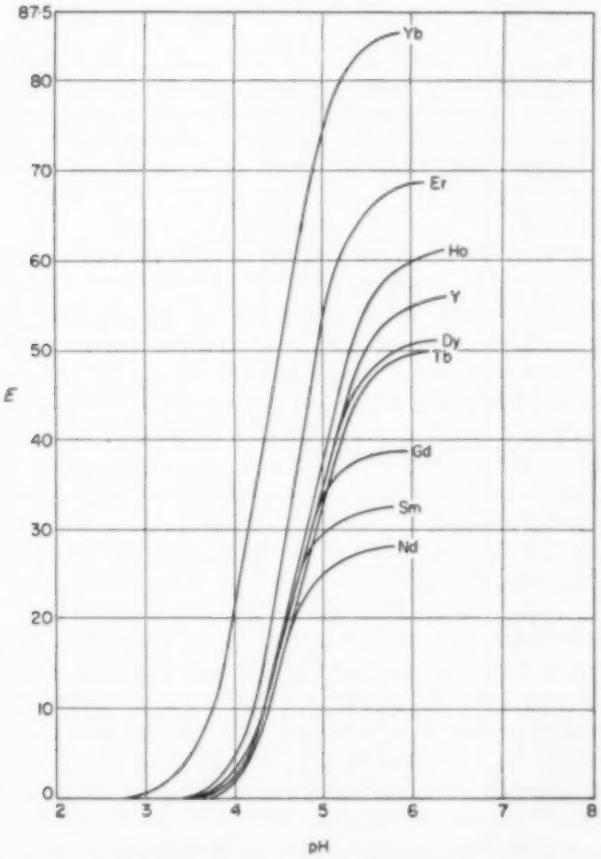

FIG. 1.—Extraction of the rare earth acetylacetonates as a function of pH.

A Beckman model DK-2 recording spectrophotometer was used for spectrophotometric measurements.

A Beckman model G pH meter was used for pH measurements and for potentiometric measurements. A J-type mercury electrode served as the indicator electrode in the potentiometric titrations.[8]

[6] D. DYRSSEN and V. DAHLBERG, *Acta Chem. Scand.* **7**, 1186 (1953).
[7] J. F. STEINBACH and H. FREISER, *Analyt. Chem.* **25**, 881 (1953).
[8] J. S. FRITZ, M. J. RICHARD and S. K. KARRAKER, *Analyt. Chem.* **30**, 1347 (1958).

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Eriochrome Black T was the indicator for the volumetric titrations. A standard solution of EDTA was the titrant in both the potentiometric and volumetric titrations.[9,10]

All other reagents were analytical reagent grade.

Procedure

The rare earth acetylacetonates were prepared by the method of QUILL *et al.*[11] Acetylacetonates were also prepared by extracting an aqueous solution of the rare earth chloride, nitrate or perchlorate with acetylacetone, and evaporating the solvent after separating the phases. After recrystallization from 95 per cent ethanol the products obtained by the two methods had similar melting points and carbon and hydrogen analyses. POPE has shown that these compounds are monohydrates when prepared by these methods.[12]

TABLE 1.—DATA USED FOR THE PLOT OF pH VS. % METAL EXTRACTED, E, SEEN IN FIG. 1

Yb		Er		Ho		Dy		Y		Tb		Gd		Sm		Nd	
pH	E	pH	E	pH	E	pH	E	pH	E	pH	E	pH	E	pH	E	pH	E
4·35	37·7	4·10	4·5	4·14	2·5	3·62	0·0	4·15	5·7	3·62	0·0	3·75	0·0	4·40	7·3	4·06	3·2
4·45	41·6	4·20	16·2	4·30	12·7	4·11	4·0	4·28	11·4	4·30	10·2	4·49	14·0	4·45	8·0	4·08	0·6
4·50	61·3	4·35	16·2	4·40	10·1	4·19	4·7	4·40	15·1	4·50	14·3	4·55	18·3	4·52	21·7	4·30	7·1
4·57	43·9	4·42	20·0	4·40	11·2	4·55	16·3	4·41	11·4	4·51	16·4	4·60	19·3	4·15	5·7	4·30	14·6
4·58	64·1	4·45	19·5	4·50	19·4	4·82	31·2	4·78	28·9	4·59	18·4	4·61	19·5	4·40	15·1	4·60	17·0
4·60	64·1	4·51	22·3	4·62	21·8	4·86	28·8	4·84	31·2	4·72	20·0	4·68	24·4	4·28	11·4	4·82	15·4
4·62	65·9	4·52	27·3	4·52	15·0	4·92	33·6	4·89	30·2	4·91	25·6	4·72	23·5	4·78	28·9	4·80	22·3
4·69	56·9	4·55	24·3	4·60	19·0	4·93	30·0	4·97	34·0	4·92	27·0	4·81	28·5	4·89	30·2	5·42	25·5
4·72	68·6	4·62	26·0	4·65	25·0	5·15	39·0	5·70	52·9	5·00	33·4	4·88	28·5	5·32	30·8	5·55	27·5
4·80	70·4	4·66	27·5	4·77	25·7	5·32	45·8			5·35	43·9	4·92	34·6	5·55	32·0	5·63	30·0
4·90	65·9	4·70	33·2	4·99	31·8					5·50	45·9	5·22	36·0				
4·95	63·1	4·72	33·8	4·72	26·2					5·70	48·0	5·70	38·0				
5·01	68·0	4·73	36·4	5·00	34·7							5·82	39·3				
5·20	82·1	4·78	38·2	5·10	40·4												
5·75	83·9	4·82	41·5	5·20	43·6												
5·79	84·6	4·85	43·8	5·45	48·5												
		4·95	45·0	5·75	57·5												
		4·98	51·7	7·08	39·5												
		5·15	57·8														
		5·49	65·5														
		7·10	60·0														

Extractions as functions of pH were studied in the conventional manner.[7] The organic phase was analysed after extraction either by spectrophotometric measurements or by dissolving a portion of the acetylacetone phase in a suitable volume of water and performing a chelometric titration either potentiometrically or with a colour indicator. The extraction curves were determined by at least two of the three methods and the results were essentially identical. Specifically, the erbium and holmium curves were obtained by spectrophotometric, potentiometric and volumetric methods. The neodymium, samarium, gadolinium, terbium, dysprosium, yttrium and ytterbium curves were obtained by potentiometric and volumetric titrations.

The pH of the water phase was measured after extraction. Buffered solutions were not used; so the possibility of extracting species other than the trisacetylacetonato rare earth(III) chelate was eliminated.

The extraction curves for the rare earth acetylacetonates are shown in Fig. 1, obtained from the data in Table 1. These curves probably were obtained under equilibrium conditions since the same curves resulted despite variations in equilibration time and concentration of rare earth. Also they are independent of the analytical method since spectrophotometric methods and EDTA titrations yielded identical curves. Fig. 2 shows the decrease in the maximum extraction of these chelates with increasing ionic radii of the central metal ion.

Determinations of the approximate solubility of the rare earth acetylacetonates were made by saturating 25 ml of water-saturated acetylacetone with the chelate at room temperature. After filtering, an aliquot portion of the filtrate was titrated with standard EDTA solution. The plot of log solubility vs. the ionic radii of the rare earths is linear as shown in Fig. 3. There is approximately

[9] A. J. BARNARD JR., W. C. BROAD and H. FLASCHKA, *Chem. Anal.* **45**, 86, 111 (1956).
[10] A. J. BARNARD JR., W. C. BROAD and H. FLASCHKA, *Chem. Anal.* **46**, 18, 46, 76 (1957).
[11] L. L. QUILL, J. G. STITES and C. N. MCCARTY, *J. Amer. Chem. Soc.* **70**, 3142 (1948).

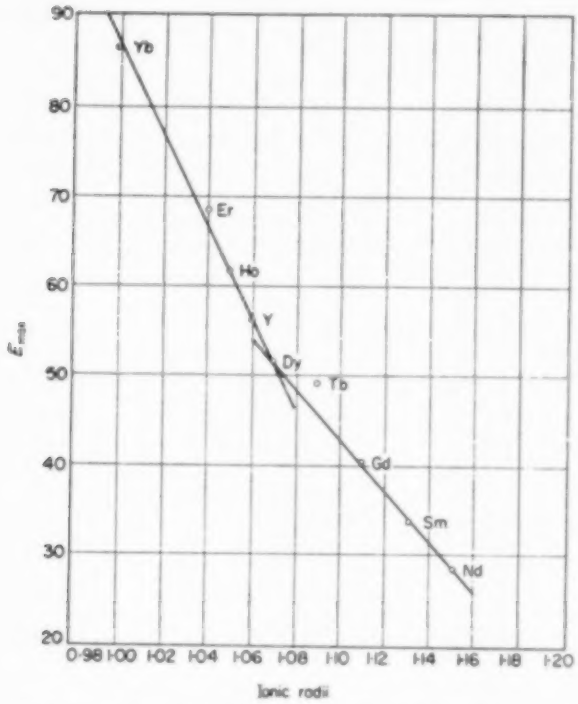

FIG. 2.—Maximum extraction of the rare earth acetylacetonates as a function of the ionic radii.

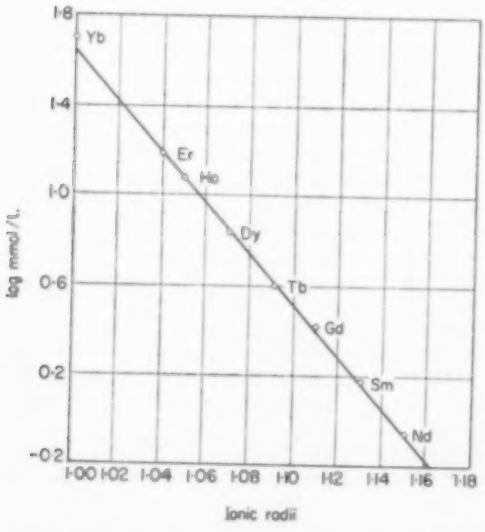

FIG. 3.—Solubility of the rare earth acetylacetonate in acetylacetone as a function of ionic radii.

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a 100-fold increase in the solubility of these chelates from neodymium to ytterbium. POPE is determining more precisely the solubility of these chelates in various solvents.[18]

DISCUSSION

Certain features of the curves in Fig. 1 are easily explained. Since it is known that more stable chelates extract at lower pH values, it would be predicted that the heavier lanthanides would be extracted at lower pH, and the curves of Fig. 1 bear this out.

Fig. 1 also shows that there is a stepwise increase in the maximum percent extracted going from neodymium (at. no. 60) to ytterbium (at. no. 70). Variation in the maximum per cent extracted can be attributed either to changes in the extent of hydrolysis or to changes in the solubility of the chelates. Since ytterbium has the smallest ionic radius it might be expected to exhibit the largest amount of hydrolysis and the smallest maximum per cent extraction. However, the reverse was observed, and it is probable that the variation in the maximum per cent extraction is caused by solubility differences, or more precisely, by differences in the partition coefficients of the chelates. Fig. 3 shows that there is a regular increase in the solubility of the chelates as the atomic number increases.

The pH at which extraction occurs is governed by the partition coefficient as well as the formation constant of the chelate; chelates with higher partition coefficients extract at lower pH values. Since the heavier lanthanides have higher formation constants as well as higher partition coefficients their extraction curves are shifted to lower pH values, while the extraction curves of the lighter lanthanides with smaller formation constants are shifted to higher pH values. Fig. 1 shows a spread of nearly one pH unit between neodymium and ytterbium. This spreading, caused by a favourable combination of solubility and formation constant, is analogous to the situation encountered in ion exchange techniques in which the heavier lanthanides are adsorbed less strongly by the resin and eluted more readily by a complexing agent. Solvent extraction may thus afford correspondingly good separation when an optimum system is found. The proximity of the extraction curves of Fig. 1 in the region between pH 4 and pH 5 limits separation by pH control alone. Extraction of the lanthanides at a pH below the pH of maximum extraction would produce little or no separation among the metals lighter than erbium. However, above a pH of about 5·3 there is a considerable difference in the per cent extracted, and counter-current extraction of an acetylacetone–water system buffered at a pH of about 5·5 should permit separation.

The curves of Fig. 1 show only the per cent extracted and do not indicate the amount which may be present before precipitation begins. There is a larger difference in extractability than indicated by Fig. 1. Acetylacetonates lighter than samarium have very limited solubility in acetylacetone (1·0 g/l.) while those heavier than samarium have greatly increased solubility (up to 26 g/l.). Hence there is a marked difference in the solubility and extractability of the acetylacetonates which seems surprising in view of the chemical similarities of the lanthanides.

Hydrate formation may account for the unexpectedly large differences in the extractability of the lanthanides by acetylacetone. It is known that the acetylacetonates of the rare earths hydrate easily, and hydrated chelates are usually less soluble than the anhydrous form. Since the ions of the heavier rare earths are smaller the methyl

[18] G. POPE. Unpublished work, Department of Chemistry, University of Kentucky, Lexington, Kentucky (1959).

groups of an octahedral acetylacetone complex would be closer and perhaps hinder the attachment of water. Hence variation of the stability and solubility of the hydrate may account for the large differences in extractability. FEIGL has suggested hydration as an explanation of the solubility of the oxinates.[13] However, other investigators have not been in agreement.[6,14]

An interesting comparison may be made between the thenoyltrifluoro acetone system[15,16] and the acetylacetone system for rare earth extraction. The chelates of these systems would be expected to behave similarly. However, chelates of β-diketones such as T.T.A. and dipivaloylmethane have relatively little difference in solubility throughout the lanthanide group, and also seem to be much more soluble in organic solvents than the acetylacetonates. Probably the acetylacetonates are able to form hydrates whereas more highly substituted β-diketones, which may be considered as substituted acetylacetonates have additional, bulky groups which sterically hinder the attachment of water to the chelate molecule. The rare earth acetylacetonates may form hydrates similar in structure to that reported for the chloroformate of iron(III) acetylacetonate.[17]

A previous report[2] indicated that tetravalent actinides may be separated from the lanthanides by extraction with acetylacetone. Hexone, chloroform and benzene were used as the solvent in this case. Apparently the acetylacetonates are more soluble in pure acetylacetone than they are in some mixed solvent systems. Another advantage of using pure acetylacetone is that the high reagent concentration limits hydrolysis.

Thus it appears that the lanthanides might be separated by solvent extraction with acetylacetone by buffering the solution in the region of maximum per cent extraction where variations in the solubility and partition coefficients of the rare earth acetylacetonates are large.

Acknowledgement—The authors express their gratitude to the Atomic Energy Commission for support of this work on Contract No. AT(40-1)2124.

[13] F. FEIGL, *The Chemistry of Specific, Selective and Sensitive Reactions*. Academic Press, New York (1949).
[14] L. POKRAS, M. KILPATRICK and P. M. BERNAYS, *J. Amer. Chem. Soc.* **75**, 1254 (1953).
[15] E. SHEPERD and W. W. MEINKE, AECU-3879 (1958).
[16] J. F. SUTTLE and T. K. KEENAN, *J. Amer. Chem. Soc.* **76**, 2184 (1954).
[17] J. F. STEINBACH and J. H. BURNS, *J. Amer. Chem. Soc.* **80**, 1839 (1958).

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J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 125 to 137. Pergamon Press Ltd. Printed in Northern Ireland

DIE VORGÄNGE BEI DER GEWINNUNG VON URAN AUS PHOSPHORSÄURE

F. HABASHI
Aus dem Institut für anorganisch chemische Technologie, Technische Hochschule Wien

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Zusammenfassung—Uran wird aus phosphorsauren Lösungen durch Octylpyrophosphorsäure verdünnt mit n-Hexan sehr rasch extrahiert. Aus verdünnten phosphorsauren Losungen, hohe Verteilungskoeffizienten werden beobachtet, aus konzentrierteren Lösungen dagegen kleine. Eine Verminderung der Wasserstoffionenkonzentration von gleich starken Phosphatlösungen bewirkt starke Erhöhung des Verteilungskoeffizienten. Diese Tatsachen, sowie die anderen experimentellen Befunde, wie die Änderung des Verteilungskoeffizienten durch Änderung der Phosphorsäure- und der Urankonzentration in der wässrigen Phase oder durch Änderung der Extraktionsmittelmenge werden eingehend diskutiert. Die verschiedenen Einflüsse auf den Verteilungskoffizienten werden auf das Vorliegen von je nach pH und Phosphorsäurekonzentration verschiedenen Uranylphosphatkomplexen in der wässrigen Lösung und der Bildung eines Komplexes zwischen Uranylion und Octylpyrophosphorsäure in der organischen Phase zurückgeführt.

Abstract—Uranium is extracted very rapidly from phosphoric acid solutions by octyl pyro phosphoric acid diluted with n-hexan. From dilute phosphoric acid solutions, high distribution coefficients are observed, whereas from concentrated solutions low distribution coefficients. Decreasing the hydrogen ion concentration from equally concentrated phosphate solutions increases greatly the distribution coefficients. These facts as well as the other experimental results, as changing the distribution coefficient by changing the phosphoric acid concentration and the uranium concentration in the aqueous phase, or through changing the quantity of the solvent are thoroughly discussed. The different factors influencing the distribution coefficients are attributed to the different uranyl phosphate complexes existing in the aqueous phase with respect to the pH and the phosphoric acid concentration, and a complex between the uranyl ion and the solvent in the organic phase.

I. EINLEITUNG

OBWOHL Uran jetzt schon in industriellem Ausmass in U.S.A. aus technischer Phosphorsäure durch Solvent Extraktion gewonnen wird,[1] gibt es doch noch keine veröffentliche Literatur, die diesen Prozess in der Gesamtheit beschreibt. In der ersten Konferenz zur friedlichen Verwendung der Atomenergie in Genf 1955, berichteten LONG *et al.*[2] zum ersten Male über die Verwendung organischer Lösungsmittel nämlich Octylpyrophosphorsäure (in folgenden als OPPA bezeichnet), zur Extraktion von Uran aus technischer Phosphorsäure. In der zweiten Konferenz (Genf 1958), wurde der einzige Bericht über diese Thema von STOLZ[3] gegeben. Er enthält jedoch keine grundlegend neue Information. Daher wurden im Rahmen der vorliegenden Arbeiten weitere Untersuchungen auf diesem Gebiet durchgeführt, auf dem es, wie ersichtlich, noch an Literatur mangelt.

Untersucht wurden in erster Linie die Verhältnisse bei der Extraktion des Urans aus Phosphorsäure mittels OPPA. Es wurden die Verteilungskoeffizienten des Urans und einiger anderer Metalle, die ebenfalls in Rohphosphaten vorkommen, bestimmt.

[1] B. F. GREEK, O. W. ALLEN und D. E. TYNAN, *Industr. Engng. Chem.* **49**, 628 (1957).
[2] R. S. LONG, D. A. ELLIS and R. H. BAILES, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 8, pp. 77–80. United Nations, New York (1956).
[3] E. M. STOLZ, JR., *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper P/1066.

Eingehend wurde auch der Einfluss der Konzentration des Extraktionsmittels, der Einfluss von Fremdionen auf das Verteilungsgleichgewicht und die Geschwindigkeit der Gleichgewichteinstellung untersucht.

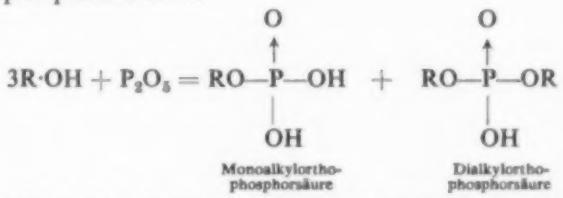
II. PHOSPHATESTER ALS EXTRAKTIONSMITTEL FÜR URAN[4]

Die Produkte der Reaktion zwischen Alkoholen und P_2O_5 sind Phosphatester. Das Verhältnis der reagierenden Stoffe bestimmt die Estertype:

(1) Neutrale Phosphatester, wie z.B. Tributylphosphat $(C_4H_9O)_3PO$, welches zur Extraktion von Uran aus Salpetersäuren Lösungen verwendet wird.

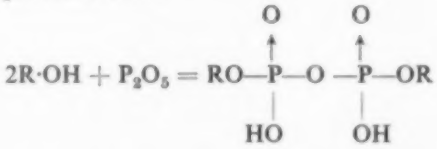
(2) Saure Phosphatester,

(i) Orthophosphorsäureester



Ein Beispiel der Monoalkylorthophosphorsäure ist Dodecylphosphat (DDPA) welches zur Extraktion von Uran aus Schwefelsäure Lösungen oft verwendet wird.

(ii) Pyrophosphorsäureester



Ein Beispiel ist Octylpyrophosphorsäure (OPPA), welches zur Extraktion von Uran aus Phosphorsäure verwendet wird. Die Stabilität des OPPA hängt stark von der Darstellungsmethode ab. Verschiedene Autoren haben verschiedene Methoden zur Darstellung dieser Ester beschrieben. Vor kurzem wurde eine Untersuchung[5] durchgeführt um die Variablen während der Darstellung zu ermitteln. Wenn P_2O_5 zuerst in Verdünnungsmittel aufgeschlämmt und dann der Alkohol hinzugefügt wird, so ist der Ester nur einige Tage stabil.[2] Wenn aber der Alkohol zuerst zum Verdünnungsmittel hinzugefügt wird und dann erst P_2O_5, so bleibt der Ester wenigstens 6 Wochen stabil.[4] Feuchtigkeit soll während der Darstellung vollig vom System fern gehalten werden und die Temperatur 15°C nicht übersteigen.

III. EXPERIMENTELL

Nach dieser letzteren Methode[5] wurde für alle eigene Arbeit benötigten Mengen an Extraktionsmittel immer frisch hergestellt. Alle Versuche wurde mit n-Hexan als Verdünnungsmittel für OPPA durchgeführt. n-Hexan chemisch rein Siedepunkt

[4] Siehe zum Beispiel G. M. KOSOLOPOFF, *Organo-Phosphorus Compounds*. John Wiley, New York (1950).
[5] USAEC Report RMO-2030 (1955).

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69°C wurde vor Gebrauch mit P_2O_5 getrocknet. Sekundärer Octylalkohol $C_8H_{17}\cdot OH$ Spez. Gew. 0·818 wurde vor Gebrauch mit $CaCl_2$ (anhyd.) getrocknt.

Als wässrige Phase wurde Testlösungen aus Uran (Milligramm Mengen) und p.a. Phosphorsäure verwendet. Der Verteilungskoeffizient (=Konzentration des Urans in der organische Phase/Konzentration des Urans in der wässrige Phase) wurde bestimmt,[6] in dem die organische mit der wässrigen Phase in einem Scheidetrichter bei hinreichend konstanter Raumtemperatur so lange zusammen geschüttelt wurde,

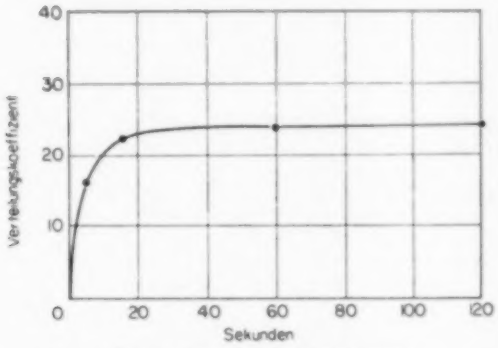

FIG. 1.—Der Verteilungsgleichgewicht.
Wässrige Phase : 6 M H_3PO_4
Anfangskonzentration des Urans : 0·4 mg/ml
Organische Phase : 2% OPPA in n-Hexan
Verhältnis wässrige/organische Phase : 10.

bis das Gleichgewicht erreicht war. Hernach wurde gewartet, bis sich die beiden Phasen wieder getrennt hatten und dann ein aliquoter Teil der wässrigen Phase auf seinen Urangehalt analysiert. Das Uran wurde kolorimetrisch nach der Thiocyanatmethode wie sie von NELSON und HUME[7] beschrieben ist, nach Phosphorsäure Abtrennung,[8] bestimmt.

IV. DER VERTEILUNGSGLEICHGEWICHT

Vorerst wurde die Geschwindigkeit der Gleichgewichtseinstellung ermittelt indem eine phosphorsaure Uranlösung verschiedene Zeiten mit dem Extraktionsmittel geschüttelt wurde. Es zeigte sich (siehe Fig. 1), dass das Gleichgewicht in 1 Min erreicht ist. Alle folgenden Extraktionsversuche wurden mit der zu Gleichgewichtseinstellung sicher ausreichenden Schütteldauer von 2 Min durchgeführt.

V. EINFLUSS DER ZEIT AUF DIE AKTIVITÄT VON OPPA IN BEZUG AUF DIE URANEXTRAKTION

Da bekannt ist, dass OPPA im Laufe der Lagerung an Aktivität verliert, wurde der Verteilungskoeffizient zwischen Uranphosphorsäure-Lösung und OPPA, das verschiedenen lange Zeit gelagert war, gemessen. Zu diesem Zweck wurde OPPA in einer Liter-Flasche mit geschliffenem Glasstöpsel aufbewahrt, aus der laufend Proben

[6] Siehe zum Beispiel G. H. MORRISON und H. FREISER, *Solvent Extraction in Analytical Chemistry*. John Wiley, New York (1957).
[7] C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, p. 104. McGraw-Hill, New York (1950).
[8] Grössere Menge Phosphorsäure stört die Farbbildung. Siehe F. HABASHI: Der Einfluss von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat, *Talanta* 2, 380 (1959).

zu Versuchszwecken entnommen wurde. Siehe Fig. 2. Die Versuche zeigten, dass OPPA schon nach 4 wochigen Lagern die Hälfte seiner Aktivität verliert. Nach etwa 18 Wochen nimmt es überhaupt kein Uran mehr auf.

VI. EINFLUSS DER OPPA-KONZENTRATION

Die Extraktion von Uran wurde bei verschiedenen Konzentrationen von OPPA in Hexan bestimmt. Bei über 25% OPPA in Hexan war die organische Phase so zäh,

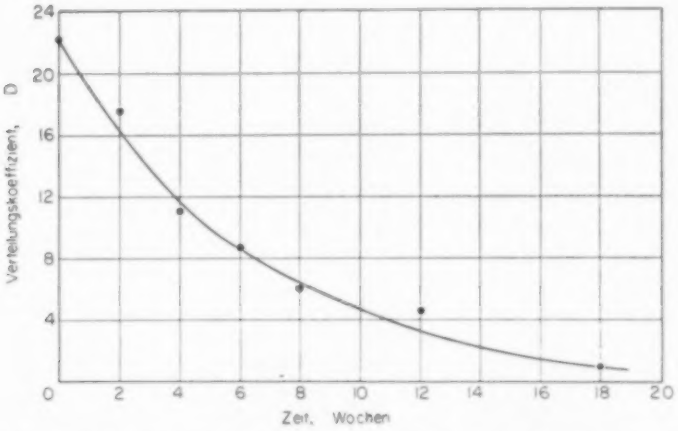

FIG. 2.—Einfluss der Zeit auf die Aktivitat von OPPA in Bezug auf die Uranextraktion.
Wässrige Phase : 6 M H_3PO_4
Anfangskonzentration des Urans : 0·4 mg/ml
Organische Phase : 2% OPPA in Hexan
Verhältnis wässrige/organische Phase : 10.

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dass sie zur Durchführung von Versuchen zur Bestimmung der Verteilung ungeeignet war. Nur bei niederen OPPA Konzentration kann der Verteilungskoeffizient von Uran als linear betrachtet werden. Siehe Fig. 3. So bleibt bei Erhöhung der OPPA-Konzentration in der organischen Phase die extrahierte Menge Uran bei hoher OPPA-Konzentration hinter der Erwartung zurück.

VII. EINFLUSS DER PHOSPHORSÄUREKONZENTRATION

Es wurde die Extraktion von Uran(VI) aus wässrigen Lösungen mit verschieden Phosphorsäurekonzentrationen durch 2% OPPA bestimmt.
Anfangskonzentration des Urans : 0·4 mg/ml
Verhältnis wässrige/organische Phase : 10

Wie zu ersehen (Fig. 4), begünstigt niedrige Prosphorsäurekonzentration die Extraktion des Urans durch OPPA. Das ist verschieden von der Extraktion von Uran aus Salpetersäure durch Äther[9] oder Tributylphosphat,[10] aber ähnlich wie die Extraktion von Uran aus Schwefelsäure durch aliphatische Amine.[11]

[9] R. BOCK und E. BOCK, *Z. Anorg. Chem.* **263**, 146 (1950).
[10] H. A. C. MCKAY, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, pp. 314–317. United Nations, New York (1956).
[11] C. F. COLEMAN, K. B. BROWN JR, J. M. MOORE und K. A. ALLEN, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper P/510.

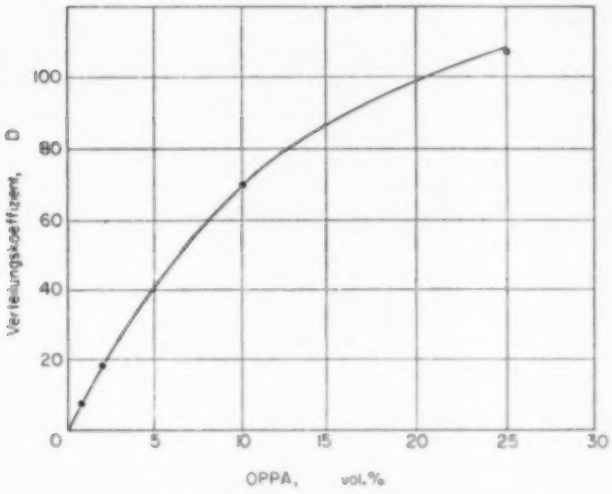

FIG. 3.—Einfluss der OPPA-Konzentration.
Wässrige Phase : 6 M H_3PO_4
Anfangskonzentration von Uran : 0·4 mg/ml
Verhältnis wässrige/organische Phase : 10.

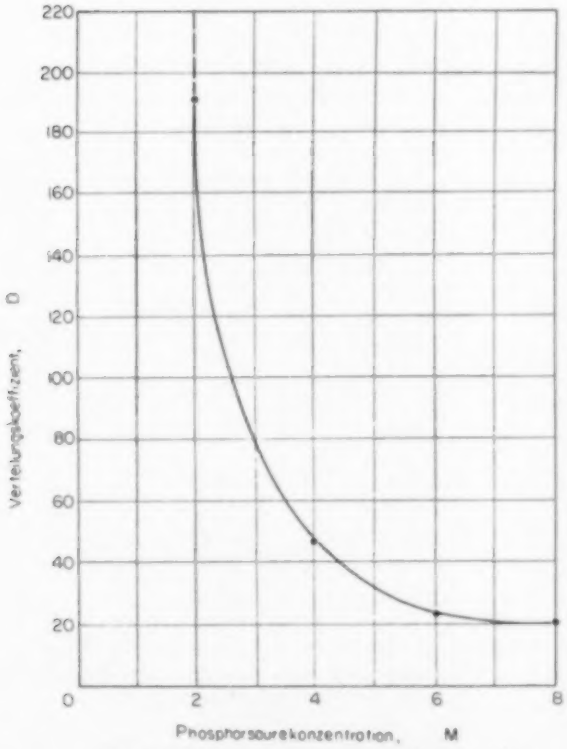

FIG. 4.—Einfluss von Phosphorsäure-konzentration.

Extraktion von Uran(IV)

Ein Teil der Stammlösung wird mit einer geringen Menge Zinkstaub reduziert bis die Lösung grün ist, und alles Uran als U (IV) vorliegt. Aus dieser Lösung werden durch Hinzufügung von Phosphorsäure Versuchslösungen mit konstanter Uran- aber

TABELLE 1.—EXTRAKTION VON URAN (IV)
Anfangskonzentration des Urans : 0·4 mg/ml
Verhältnis wässrige/organische Phase 10

H_3PO_4 (M)	Wässrige Phase $[U(IV)]_a$	Organische Phase $[U(IV)]_o$	Verteilungskoeffizient
1	(Uran fällt aus)		
2	0·140	2·60	18·6
4	0·165	2·35	14·2
6	0·170	2·30	13·5

verschiedener Phosphorsäurekonzentration bereitet und die Verteilungskoeffizienten für 2% OPPA bestimmt. Siehe Tabelle 1. Im Vergleich mit früheren Versuchen (Fig. 4), zeigt es sich, dass Uran (IV) wesentlich schwächer extrahiert wird als Uran (VI).

VIII. EINFLUSS DER URANKONZENTRATION

Das System Phosphorsäure–Uranlösung–OPPA in Hexan weicht, wie zu erwarten, stark vom idealen Verhalten ab. Mit steigender Urankonzentration in der wässrigen phosphorsauren Lösung fällt der Verteilungskoeffizient, wie in Tabelle 2 und Fig. 5

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TABELLE 2.—EINFLUSS DER URANKONZENTRATION
Wässrige Phase : 8 M H_3PO_4
Organische Phase : 2% OPPA in Hexan
Verhältnis wässrige/org. 10

Anfangskonzentration von Uran (mg/ml)	Wässrige Phase $[U]_a$	Organische Phase $[U]_o$	Verteilungskoeffizient
0·4	0·125	2·75	22·0
0·6	0·190	4·10	21·6
0·8	0·320	5·00	15·7
1·0	0·430	5·70	13·3
1·2	0·520	6·80	13·1
2·0	1·100	9·00	8·2

dargestellt ist. Die Abnahme des Verteilungskoeffizienten des Urans in diesem Fall ähnelt dem Verhalten des Urans mit Tributylphosphat aus Salpetersäure, ist aber verschieden von der Extraktion durch Äther und Alkohole.[12]

[12] J. M. FLETCHER, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 1, pp. 459. United Nations, New York (1956).

IX. EINFLUSS VON ANIONEN UND WASSERSTOFFIONENKONZENTRATION

Die Verteilung wird durch die Anwesenheit von Sulfaten nicht, durch Chloride und Nitrate wenig, stark dagegen durch Fluoride abnehmen. Zugesetztes Trinatriumphosphat erhöht den Verteilungskoeffizienten stark. Die Erhöhung des Verteilungskoeffizienten ist wahrscheinlich auf die Reaktion

$$2H_3PO_4 + Na_3PO_4 = 3NaH_2PO_4$$

zurückzuführen, welche die Wasserstoffiionenkonzentration der wässrigen Lösung vermindert. Um dies nachzuweisen wurden die gleichen Versuche mit äquivalenten

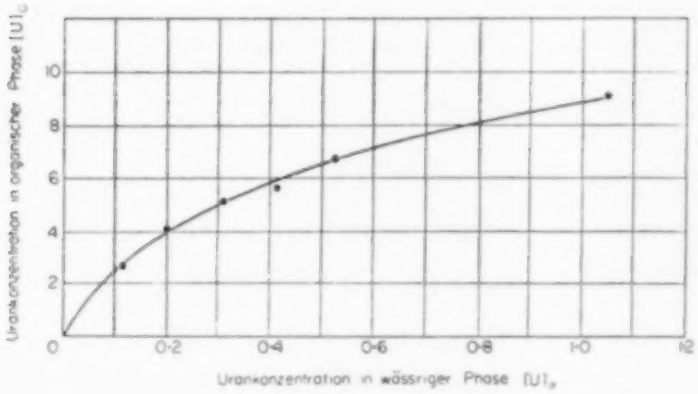

FIG. 5.—Der Verteilungs-Isotherm.

Mengen NaOH anstelle von Na_3PO_4, wiederholt. Wiederum wurde eine Erhöhung des Verteilungskoeffizienten beobachtet. Siehe Fig. 6. Dies kann also auf die Erhöhung des pH-Wertes der Lösung zurück geführt werden, und soll später eingehend diskutiert werden.

X. EXTRAKTION DER BEGLEITMETALLE

Eisen

Da Eisen in technischer Phosphorsäure zwischen 4 und 6 g/l., das ist etwa 200 mal so viel wie Uran, enthalten ist, wurde auch seine Extraktion durch OPPA untersucht. Es wurde sowohl der Verteilungskoeffizient von Fe(II) und Fe(III) bei verschiedenen H_3PO_4-Konzentrationen bestimmt. Wie man aus Fig. 7 sieht, wird Fe(II) durch OPPA praktisch nicht extrahiert, während Fe(III) sehr stark extrahiert wird.

Vanadium

Da Vanadium in Phosphatgestein in der Grössenordnung von etwa 0·1% vorkommt, wurde sein Extrahierbarkeit durch OPPA untersucht. Die auf übliche Weise durchgeführten Extraktionsversuche zeigten, dass Vanadium (V) überhaupt nicht extrahiert wird, jedoch wurde festgestellt, dass eine merkliche Extraktion erreicht werden konnte, wenn Vanadium zum V(IV) reduziert wurde. Siehe Fig. 8.

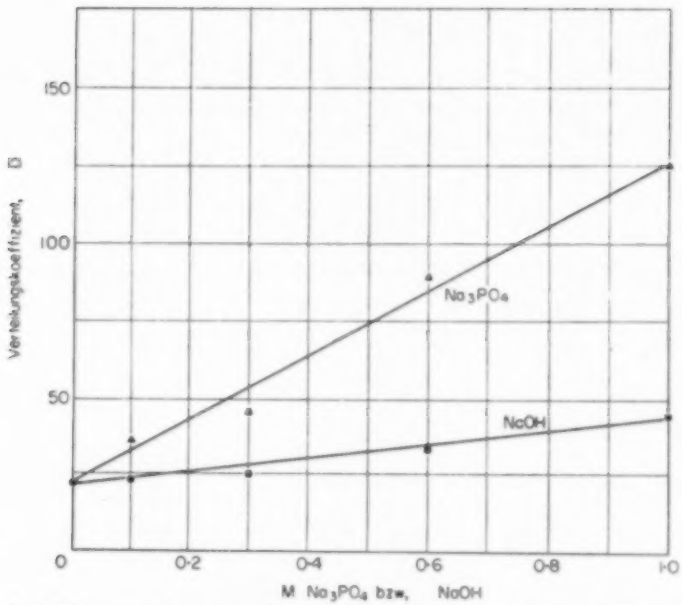

FIG. 6.—Einfluss von Zugesetztem Trinatriumphosphat bzw. der Wasserstoffionenkonzentration.
Verhältnis wässrige/organische Phase : 10
Wässrige Phase : 0·4 mg/ml in 6 M H_3PO_4
Organische Phase : 2% OPPA in n-Hexan.

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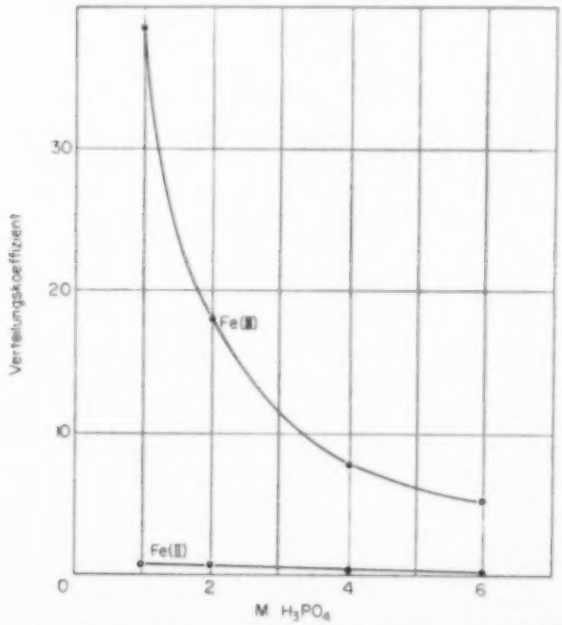

FIG. 7.—Extraktion von Eisen aus H_3PO_4-Lösungen durch OPPA
Wässrige Phase : 0·4 mg Fe/ml
Organische Phase : 2% OPPA in n-Hexan
Verhältnis wässrige/organische Phase : 10.

Thorium

Da auch Thorium immer zusammen mit Uran in Erzen und Gesteinen auftritt, war es auch interessant die Extrahierbarkeit von Thorium durch OPPA aus Phosphorsäurelösungen zubestimmen. Es wurde gefunden, dass Thorium merklich extrahiert wird. Siehe Fig. 9.

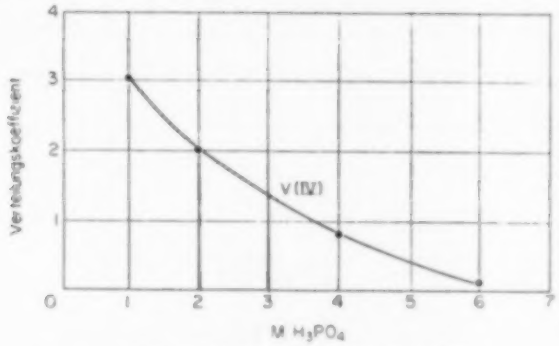

FIG. 8.—Verteilung von Vanadium (IV).
Anfangskonzentration von Vanadium : 0·4 mg/ml
Organische Phase : 2% OPPA in n-Hexan
Verhältnis wässrige/organische Phase : 1/1.

Cer

Wie Thorium wird auch Cer in beiden Wertigkeitstufen von OPPA aufgenommen wobei Ce(III) einen höheren Verteilungskoeffizient als Ce(IV) hat. Die Abhängigkeit des Verteilungskoeffizienten von der Phosphorsäurekonzentration ist jedoch verschieden von der des Urans, des Thoriums, des Vanadiums und des Eisens. Hier wird ein Maximum bei 4 M H_3PO_4 beobachtet, wie aus Fig. 10 zu entnehemen ist.

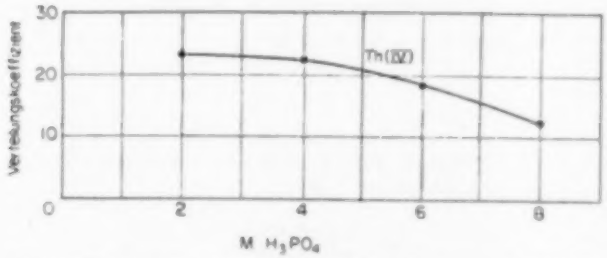

FIG. 9.—Verteilung von Thorium zwischen H_3PO_4-Lösungen und 2% OPPA in Hexan.
Anfangskonzentration von Thorium : 0·4 mg/ml
Verhältnis wässrige/organische Phase : 10.

XI. DISKUSSION DER ERGEBNISSE

Urankomplexe in Phosphorsäure

Wie schon im Teil VII gezeigt wurde, hat die Konzentration der Phosphorsäure einen bedeutenden Einfluss auf die Extraktion des Urans. Bei geringen Phosphorsäurekonzentrationen wird das Uran stark extrahiert, während es bei hohen Säurekonzentrationen nur wenig extrahiert werden kann. Es scheint deshalb, dass das Uran in der konzentrierten Säure in einer nicht extrahierbaren Form gebunden

ist. Wenn man annimmt, dass die Komlexverbindung zwischen UO_2^{2+} und $H_2PO_4^-$ gemäss

$$UO_2^{2+} + nH_2PO_4^- = UO_2 \cdot (H_2PO_4^{+2-n})_n \qquad (1)$$

$$k_n = \frac{[UO_2(H_2PO_4^{+2-n})_n]}{[UO_2^{2+}][H_2PO_4^-]^n}$$

vor sich geht, dann gilt für die Konzentrationen in der wässrigen Phase

$$[U_t] = [UO_2^{2+}] + \Sigma_n[UO_2(H_2PO_4^{+2-n})_n] = [UO_2^{2+}]\{1 + \Sigma_n k_n[H_2PO_4^-]^n\}$$

wo $[U_t]$ die gesamte Urankonzentration bedeutet, n durchläuft den Bereich der in

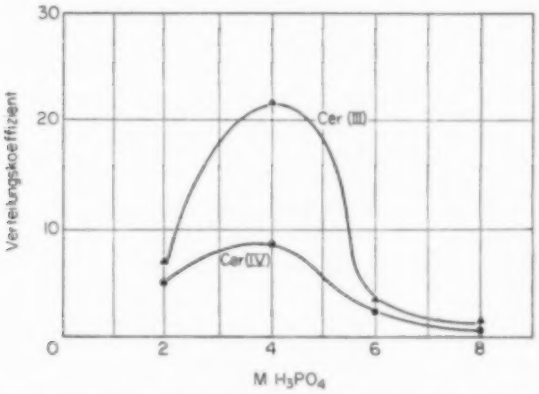

FIG. 10.—Verteilung von Cer zwischen H_3PO_4-Lösungen und 2% OPPA in Hexan.
Anfangskonzentration von Cer : 0·4 mg/ml
Verhältnis wässrige/organische Phase : 10.

Frage kommenden Liganden. Wenn nur das nicht komplexgebundene Uran extrahiert werden kann, dann ist der gemessene Verteilungskoeffizient

$$D = \frac{[UO_2^{2+}]_o}{[U_t]_a}$$

wobei o = organische und a = aqua Phase. Der Verteilungskoeffizient bei Abwesenheit eines komplexbildenden Mittels ist

$$D_o = \frac{[UO_2^{2+}]_o}{[UO_2^{2+}]_a}$$

Daher hängt der gemessene Verteilungskoeffizient von der Phosphorsäurekonzentration gemäss

$$D = D_o \frac{[UO_2^{2+}]_a}{[U_t]_a} = D_o \left\{\frac{1}{1 + \Sigma_n k_n[H_2PO_4^-]^n}\right\} \qquad (2)$$

ab. Das bedeutet, dass der gemessene Verteilungskoeffizient mit steigender Phosphorsäurekonzentration abnimmt.

Die Annahme, dass die Erminderung des Verteilungskoeffizienten bei steigender Phosphorsäurekonzentration durch die Ausbildung von Komplexen hervorgerufen

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wird, erscheint darüber hinaus auch dadurch gerechtfertigt, dass das Uran in Phosphorsäure tatsächlich viele Komplexe bildet. LEADER[13] hat als erster die Existenz eines Uranylphosphatkomplexions $UO_2H_2PO_4^+$ in der Lösung angenommen. BAES[14] bewies durch spektrophotometrische Untersuchung die Existenz dieses Komplexions sowie die der weiteren Komplexe

$$UO_2 \cdot H_3PO_4^{2+},\ UO_2(H_2PO_4)_2 \quad \text{und} \quad UO_2(H_2PO_4) \cdot H_3PO_4^+.$$

THAMER[15] stellte fest, dass Uran in verdünnten phosphorsaueren Lösungen hauptsächlich als Uranylion UO_2^{2+} enthalten ist, dass aber mit steigenden Phosphor-

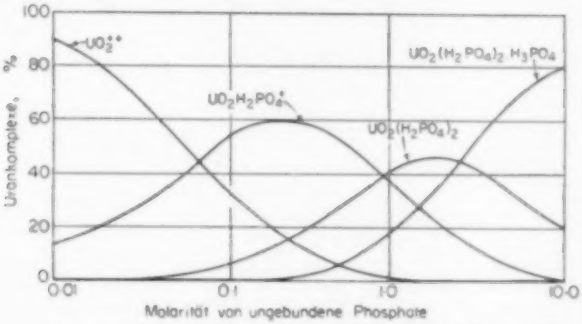

FIG. 11.—Urankomplexe in Phosphorsäure (Nach THAMER[15])

säurekonzentrationen das Uranylion verschwindet, gleichzeitig treten die Komplexe $UO_2H_2PO_4^+$ und $UO_2(H_2PO_4)_2$ auf, die auch von anderen Forschern indentifiziert wurden, bis schliesslich in konzentrierter Phosphorsäure der ungeladene Komplex $UO_2(H_2PO_4)_2 \cdot H_3PO_4$ vorherrscht. Siehe Fig. 11. Ähnliche Komplexe wurden von MARCUS[16] bei Ionenaustauschuntersuchungen gefunden. Auch SCHREYER und BAES[17] haben durch Untersuchungen über die Löslichkeit von Uranylphosphat in Phosphorsäure Umwandlungen zwischen verschiedenen Uranylkomplexen festgestellt.

Einfluss der Wasserstoffionenkonzentration auf die Uranextraktion

In der eigen Arbeit wurde experimentell gefunden (Siehe Teil IX), dass die Extraktion des Urans zunimmt, wenn die konzentrierte Phosphorsäure teilweise neutralisiert wird. Daher ist nicht allein die Molarität der Syure wie nach Gleichung 2 auf die Extraktion von Einfluss, sondern auch die Wasserstoffionenkonzentration der Lösung. Doch ist auch bei verminderter Wasserstoffionenkonzentration einer uranhaltigen konzentrierten Phosphatlösung das Uran nur in komplexgebundener Form vorhanden. Daher kann man die Erhöhung des Verteilungskoeffizienten bei teilweiser Neutralisation der Säure nicht auf Grund einer in der wässrigen Phase stattfindenden Wechselwirkung zwischen dem Uranylion und $H_2PO_4^-$, erklären. Dagegen ergibt

[13] G. R. LEADER, USAEC Report CN-295 (1944).
[14] C. F. BAES, JR., *J. Amer. Chem. Soc.* **76**, 354 (1954).
[15] B. J. THAMER, *J. Amer. Chem. Soc.* **79**, 4298 (1957).
[16] Y. MARCUS, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958. Paper P/1605.
[17] J. M. SCHREYER und C. F. BAES, JR., *J. Amer. Chem. Soc.* **76**, 354 (1954).

sich eine solche Erhöhung, wenn man eine Reaktion zwischen OPPA und dem nicht komplexgebunden Anteil Uranylion annimmt. In diesem Fall werden Spuren von Uranylionen, wenn sie aus der wässrigen Phase durch OPPA entfernt werden, sofort durch neue Uranylionen entsprechend der Verschiebung des Gleichgewichtes der Urankomplexe ersetzt. Da OPPA selbst eine Säure mit zwei beweglichen Wasserstoffatomen ist (siehe Teil II), kann die Reaktion durch

$$UO_2^{2+}{}_{(a)} + H_2X_{(o)} = UO_2X_{(o)} + 2H^+{}_{(a)} \tag{3}$$

beschrieben werden, wobei H_2X das nicht komplexgebundene OPPA in der organischen Phase bedeutet und die Indizes (a) und (o) die wässrige bzw. organische Phase bezeichnen. Für diese Reaktion gelten die Gleichungen:

$$K = \frac{[UO_2X]_{(o)} \cdot a^2_{H^+(a)}}{[UO_2^{++}]_{(a)}\,[H_2X]_{(o)}} \tag{4}$$

$$D_o = K\frac{[H_2X]_{(o)}}{a^2_{H^+(a)}} \tag{5}$$

$$D_o = \frac{[UO_2X]_{(o)}}{[UO_2^{2+}]_{(a)}} \tag{6}$$

$$D = \frac{[UO_2X]_{(o)}}{[UO_2^{2+}]_{(a)}\{1 + \Sigma_n k_n[H_2PO_4^-]^n} \tag{7}$$

$$[OPPA]_o = [H_2X]_o + [UO_2X]_o \tag{8}$$

$$[U_t]_a \cdot V_a = [UO_2X]_o \cdot V_o + [UO_2^{2+}]_a \cdot V_a\{1 + \Sigma_n k_n[H_2PO_4^-]^n\} \tag{9}$$

wobei OPPA die Gesamt-OPPA-Konzentration, V_a und V_o Volumen der organischen und wässrigen Phasen, bedeutet. Wenn also die Reaktion (3) von links nach rechts verschoben wird, wie es durch Entfernung der Wasserstoffionen aus der wässrigen Phase geschehen kann, wird mehr Uran in die organische Phase extrahiert. Dieser Befungd steht mit den Ergebnissen der Extraktionsversuche im Einklang. Ferner erklärt die Reaktion zwischen OPPA und Uranylion die weiteren bisher gefundenen experimentellen Ergebnisse:

(1) Erniedrigung des gemessenen Verteilungskoeffizienten durch Erhöhung der Urankonzentration bei konstanter OPPA Konzentration:

Für eine gegebene Gesamtmenge des OPPA in der organischen Phase verbleibt umso weniger nicht an urangebundenes OPPA (H_2X), je höher die Urankonzentration ist,

$$[H_2X]_o = [OPPA]_o - \frac{[U_t]}{\dfrac{1}{D} + \dfrac{V_o}{V_a}} \tag{10}$$

Aus Gleichungen (7) und (5) folgt weiters,

$$D = \frac{K}{1 + \Sigma_n k_n[H_2PO_4^-]^n \cdot a^2_{H^+}}[H_2X] \tag{11}$$

wobei der gemessene Verteilungskoeffizient mit wachsender Urankonzentration abnimmt, da $[H_2X]$ in diesem Fall abnimmt. Dies steht in Übereinstimmung mit den im Teil VIII beschriebenen Experimenten.

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(2) Variable OPPA Konzentration und konstante Urankonzentration:

Umgekehrt nimmt mit steigender Konzentration des ursprünglich vorhandenen OPPA auch die Menge des nicht an Urangebundenen OPPA zu. Die Zunahme ist nicht linear, da die Menge des ungebundenen OPPA nach Gleichung (10) auch noch vom Verteilungskoeffizient abhängt. Daher wird auch der Verteilungskoeffizient mit steigender OPPA Konzentration steigen, doch keine lineare Funktion der ursprünglichen OPPA Konzentration sein, wie auch schon die Experimente ergaben. (Siehe Teil VI).

Die Tatsache, dass die Extraktion des Urans verbessert wird, wenn man die Säure teilweise neutralisiert, liesse eine Abänderung der Verfahren zur Gewinnung von Uran aus Phosphaten Zweckmässig erschienen. Es ist demnach günstiger bei der Herstellung von Phosphat-Düngemitteln das Uran erst nach einer erfolgten teilweisen Neutralisation zu extrahieren. So wird man z.B. bei der Produktion von Kalium- oder Ammonphosphat nicht die primär hergestellte Phosphorsäure extrahieren, sondern erst die durch Neutralisation gewonnene Lösung der Phosphate. Dasselbe gilt für die Extraktion des Urans während der Gewinnung von Dikalziumphosphatdüngern.

Herrn Prof. Dr. H. Hohn schulde ich Dank für sein Interesse an dieser Arbeit und sein förderndes Entgegenkommen.

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EXTRACTION OF THORIUM(IV) BY DI ESTERS OF ORTHOPHOSPHORIC ACID, $(GO)_2PO(OH)$*

D. F. PEPPARD, G. W. MASON and S. MCCARTY
Argonne National Laboratory, Box 299, Lemont, Illinois

(*Received* 18 *June* 1959)

Abstract—The extraction of tracer-level Th(IV) into solutions of $(GO)_2PO(OH)$, symbolized as HDGP, in toluene as carrier solvent, where G is 2-ethylhexyl, (EH), and para(1,1,3,3-tetramethyl butyl)phenyl, (OΦ), from aqueous perchlorate, chloride and nitrate solutions has been investigated. The distribution ratio, K, has been shown to vary directly with the third power of the stoicheiometric concentration of extractant in the solvent phase (third-power solvent dependency) and inversely with the fourth power of the stoicheiometric hydrogen ion concentration in the aqueous phase (inverse fourth-power acid dependency) for the di[para(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid systems. The di(2-ethylhexyl) phosphoric acid systems display a more complicated behaviour, the K being third-power solvent dependent in each of the aqueous systems, but inverse third-power acid dependent in the nitrate systems and inverse fourth-power acid dependent in the perchlorate and chloride systems at low acidities ranging to nearly inverse third-power acid dependent at high acidities.

The extracted entities are formulated as $Th(DO\Phi P)_2[H(DO\Phi P)_2]_2$, $Th(DEHP)_2[H(DEHP)_2]_2$ and $Th(DEHP)[H(DEHP)_2]_2X$, where X is nitrate, chloride and probably perchlorate, and tentatively postulated as co-ordination complexes of co-ordination number six. The effect of the corresponding mono esters as contaminates is discussed.

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THE use of mixed n-butyl orthophosphoric acids (mole ratio of di-ester to mono-ester of 4·5 to 1) in the preferential extraction of the "yttrium group" lanthanides from the lower-Z members and in the mutual separation of zirconium and niobium in tracer-level concentration was reported by SCADDEN and BALLOU.[1] These investigators were the first to report the use of acidic esters of orthophosphoric acid in extractions involving M(III), M(IV) and M(V) metals.

PEPPARD *et al.* have described the application of di(2-ethylhexyl) orthophosphoric acid, an example of the type solvent $(GO)_2PO(OH)$, to the fractionation of the trivalent lanthanides plus yttrium,[2] to the isolation of certain carrier-free radioactive M(III) nuclides,[3] to the mutual separation of certain M(III) actinides[4] and to the separation of Bk(IV)[5] and Ce(IV)[3] from M(III) actinides and lanthanides. The nature of the extracted species involved in the extraction of selected lanthanides(III) and actinides(III) and the extractant dependencies and acid dependencies of the distribution ratios have been reported.[2,6]

Whereas, in the study of M(III) actinides and lanthanides, the expected direct third-power extractant dependencies and inverse third-power acid dependencies were realized regardless of the mineral acid employed in the aqueous phase and for both

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
[2] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[3] D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
[4] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and S. MCCARTY, *J. Inorg. Nucl. Chem.* **12**, 141 (1959).
[5] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[6] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **7**, 276 (1958).

G = 2-ethylhexyl and G = para(1,1,3,3-tetramethyl butyl) phenyl,[2,6] the corresponding investigations of M(IV) actinides and lanthanides reveal more complicated dependencies indicating competing modes of extraction. The study presently reported was concerned with the extraction of tracer-level Th(IV) from aqueous $HClO_4$, HCl and HNO_3 phases into a $(GO)_2PO(OH)$ plus carrier solvent phase.

EXPERIMENTAL

Sources of materials

Both di(2-ethylhexyl)orthophosphoric acid and di[para(1,1,3,3-tetramethyl butyl)phenyl]orthophosphoric acid were obtained in admixture with the corresponding mono ester (and presumably traces of tertiary ester and alcohol or phenol) from Victor Chemical Co. and purified as reported previously.[2,5,7] Samples of the corresponding mono esters were isolated at the same time. Tri-butyl phosphate, $(n\text{-}C_4H_9O)_3PO$, symbolized as TBP was obtained from Commercial Solvents Corporation and purified as described previously.[8] Reagent grade NaCl was recrystallized twice. For the preparation of $NaNO_3$ and $NaClO_4$, reagent grade sodium carbonate was recrystallized twice from a methanol–water mixture and the dried salt neutralized with the appropriate freshly distilled acid. The HCl was distilled just before use. α-Active 8×10^4 year ^{230}Th (^{230}Th to ^{232}Th isotope ratio of 10 to 1) was obtained from A.N.L. stocks and was freshly purified from daughter activities before use.

Nomenclature

Continuing previous usage,[4,6] employed in the interests of brevity and ease of discussion, symbolic formulae, in which H represents a theoretically ionizable hydrogen, are used. In this symbolic system the two type solvents, $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$, are represented respectively as HDGP and H_2MGP, without regard for molecular complexity, the D and M respectively signifying di and mono in reference to the number of G groups per formula. The 2-ethyl hexyl group is represented as EH and the para(1,1,3,3-tetramethyl butyl)phenyl as OΦ, i.e. octyl phenyl, so that di(2-ethylhexyl)orthophosphoric acid and di[para(1,1,3,3-tetramethylbutyl)phenyl]orthophosphoric acid are symbolized respectively as HDEHP and HDOΦP.

The distribution ratio, K, for Th(IV) is defined as the concentration of Th in the upper divided by the concentration of Th in the lower of two equilibrated liquid phases, the concentration being indicated by the α-counting rate of an aliquot.

The term "carrier solvent"[4,6,9] is used in preference to the commonly used term "inert diluent", since the effect of the diluent upon the K may be quite marked.[6,9]

Determination of distribution ratios

The distribution ratio, K, was determined radiometrically as reported previously,[6] extreme care being taken, in the determination of K values in excess of 10^3, to avoid inclusion of a trace of the upper phase when sampling the lower. All phases were pre-equilibrated before use, and all data were checked both by "direct" and "reverse" extractions. Unless otherwise stated, the carrier solvent is toluene. In tracer studies, the concentration of Th(IV) was less than 3×10^{-5} M.

Dependency studies

Each of the extractant dependency, acid dependency and inorganic anion dependency studies was made at a constant ionic strength in the aqueous phase. Studies made under other conditions were meant to supply confirmatory data only.

Determination of gross anion extraction

In the determination of the anion to thorium ratio, approximately 2 l. of extract was prepared. Following exhaustive centrifugation, the thorium and the anion under study were returned to an aqueous phase by re-extraction, using a mineral acid which would not interfere in subsequent determinations. For example, the re-extraction was performed using HNO_3 in the determination of the

[7] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 221 (1958).
[8] D. F. PEPPARD, W. J. DRISCOLL, R. J. SIRONEN and S. MCCARTY, *J. Inorg. Nucl. Chem.* **4**, 326 (1957).
[9] D. F. PEPPARD, G. W. MASON and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **10**, 117 (1959).

chloride to thorium ratios. Following scrubbing with benzene to remove residual solvent, the aqueous re-extract was suitably evaporated before being subjected to the standard techniques of analysis.

RESULTS AND CONCLUSIONS

Acid dependencies

From Fig. 1, it is seen that the K for Th(IV) into $1{\cdot}0 \times 10^{-3}$ F HDOΦP is inversely fourth-power dependent upon the hydrogen ion concentration in the aqueous phase, where the aqueous phase has a constant ionic strength of unity in nitrate, chloride or perchlorate. The relative extractability of Th(IV) is seen to increase in the order

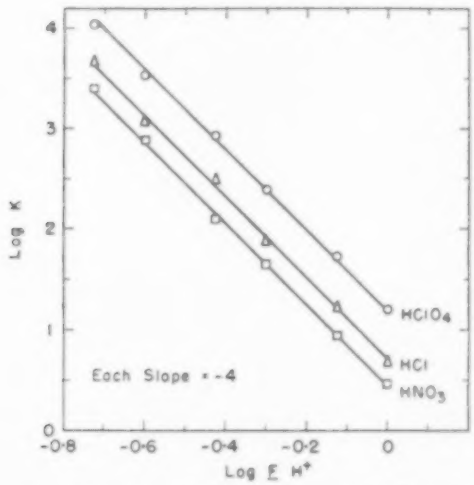

FIG. 1.—Hydrogen ion dependency of the extraction of Th(IV) into $1{\cdot}0 \times 10^{-3}$ F HDOΦP (toluene) from aqueous 1·0 F ClO_4^-, Cl^- and NO_3^- solutions. (HX + NaX, $\mu = 1{\cdot}0$.)

$K_{ClO_4^-} > K_{Cl^-} > K_{NO_3^-}$, which is the order to be expected on the basis of relative complexing of Th(IV) by ClO_4^-, Cl^- and NO_3^-, NO_3^- complexing most strongly and ClO_4^- least strongly,[10–12] on the assumption that none of the anion in question is contained in the extracted species.

The extraction of Th(IV) from aqueous phases of the foregoing composition into $3{\cdot}8 \times 10^{-2}$ F HDEHP follows a more complex law, as shown in Fig. 2. For the chloride and perchlorate cases, the limiting slopes at the lowest hydrogen ion concentrations investigated indicate inverse fourth-power hydrogen ion dependencies; but in the higher hydrogen ion concentration range these dependencies approach inverse third-power. As in Fig. 1, the perchlorate curve lies above that for chloride.

The nitrate curve, in Fig. 2, is seen to be unique in two respects: the slope approaches a limiting value of −3, rather than −4, at the low acidity range; and the curve lies far above those for chloride and perchlorate, rather than below as in Fig. 1. This behaviour is consistent with the assumption that the extracted species contains nitrate. (The extracted species in a saturated HDEHP–toluene phase, i.e. in one formed by contacting the HDEHP–toluene phase with portions of a neutral

[10] E. L. ZEBROSKI, H. W. ALTER and F. K. HEUMANN, *J. Amer. Chem. Soc.* **73**, 5646 (1951).
[11] R. A. DAY, JR. and R. W. STOUGHTON, *J. Amer. Chem. Soc.* **72**, 5662 (1950).
[12] W. C. WAGGENER and R. W. STOUGHTON, *J. Phys. Chem.* **56**, 1 (1952).

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aqueous phase containing thorium nitrate in high concentration until no further extraction occurs, has been shown to contain one nitrate group per atom of thorium.[13] However, such a species contains only three monomeric units, or their equivalent, of DEHP per atom of thorium; and the mechanism of extraction at or near saturation must be radically different from that operative in the experiments presently described.)

The change of slope of the chloride and perchlorate curves from —4 in the low-acid region to approximately —3 in the high-acid region of Fig. 2 might be considered

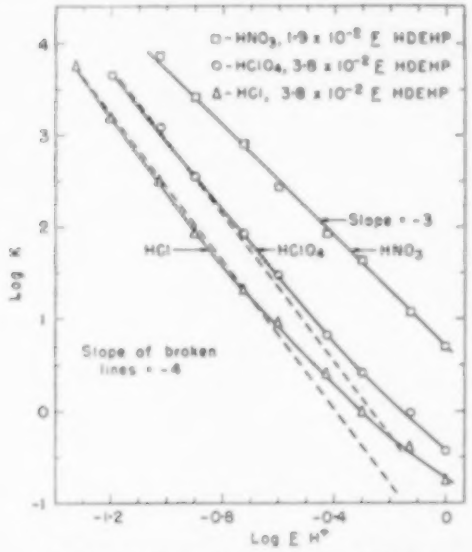

FIG. 2.—Hydrogen ion dependency of the extraction of Th(IV) into $3{\cdot}8 \times 10^{-2}$ F HDEHP (toluene) from aqueous 1·0 F ClO_4^-, Cl^- and NO_3^- solutions. (HX + NaX, $\mu = 1{\cdot}0$.)

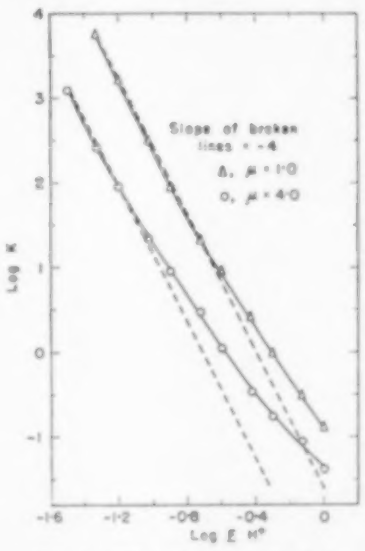

FIG. 3.—Effect of μ upon the hydrogen ion dependency of the extraction of Th(IV) into $3{\cdot}8 \times 10^{-2}$ F HDEHP (toluene) from aqueous Cl^- solutions. (HCl + NaCl, $\mu = 1{\cdot}0$ and 4·0.)

an activity coefficient effect, except that this interpretation is in conflict with the data of Fig. 1 which shows a —4 slope in the high-acid range when HDEHP is replaced by HDOΦP as extractant. By analogy with the interpretation of the nitrate data of Fig. 2, it might be assumed that in the high-acid region, the extracted species contain chloride and perchlorate respectively. The HDEHP data of Fig. 3 may be correlated with this assumption: it being noted that the departure from the —4 slope becomes noticeable at a lower acidity for the $\mu = 4$ M curve than for the $\mu = 1$ M curve and that the two curves tend to converge with increasing acidity. The distance between the two curves in the low acid range is essentially that to be expected from consideration of chloride complexing in the aqueous phase using the complexity constants of WAGGENER and STOUGHTON.[12]

Anion dependencies

In Fig. 4, the effect upon the K for Th(IV) of one-for-one substitution of the complexing nitrate ion for the lesser-complexing perchlorate ion, the nitrate ion

[13] D. F. PEPPARD and J. R. FERRARO, *J. Inorg. Nucl. Chem.* **10**, 275 (1959).

concentration being increased successively by factors of two, is seen to be opposite in sign for the two extractants studied. As the nitrate ion concentration is increased ($\mu = 1$ M, $[H^+] = 1$ M) the K decreases, with HDOΦP as extractant, the decrease being in good agreement with that predicted from a consideration of the $Th(NO_3)^{3+}$ association constant as reported by DAY and STOUGHTON,[11] on the assumption that the extracted species contains no nitrate. Likewise, the increase in K as the nitrate concentration is increased, with HDEHP as extractant, is in good agreement with

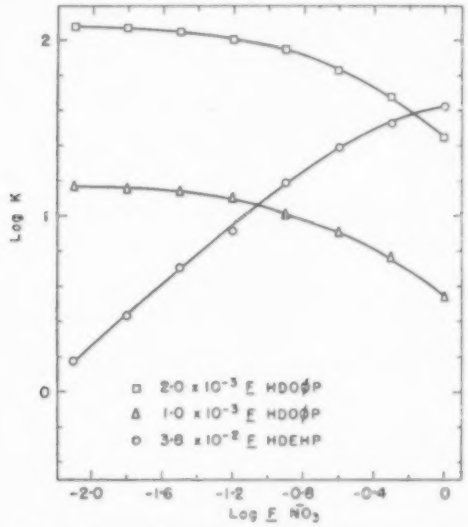

FIG. 4.—Effect of substitution of NO_3^- for ClO_4^- upon the extraction of Th(IV) into HDOΦP (toluene) and HDEHP (toluene) from aqueous $HClO_4 + HNO_3$, $\mu = 1{\cdot}0$, $[H^+] = 1{\cdot}0$.

the predicted increase, on the assumption that the predominant extracting species, under the conditions employed, contains one nitrate group per atom of Th. These effects are treated in detail in the DISCUSSION section.

Composite acid and anion dependencies

The effect of varying hydrogen ion and nitrate ion concentrations concurrently, fixing their ratio at unity, and operating at $\mu = 1$ M is shown in Fig. 5. If only nitrate complexing in the aqueous phase is involved, i.e. no nitrate in the extracted species, the plot should start at a limiting slope of -4 at low acidity and become progressively more negative with increasing acidity (i.e. with increasing nitrate concentration). The K values should, therefore, lie above the curve of Fig. 1. The HDOΦP curve is seen to vary in this manner. The HDEHP curve, however, has a limiting slope of approximately -2 in the low-acid range and the K values lie below the line from Fig. 2. A curve drawn through these points is reproduced, in its essentials, by a plot of an equation derived in the DISCUSSION section assuming competitive extraction of two species, one containing one nitrate group per atom of thorium and the other containing no nitrate.

The effect of varying hydrogen ion and chloride ion concentrations concurrently, fixing their ratio at unity and operating at $\mu = [H^+]$ is shown in Fig. 6. The HDOΦP

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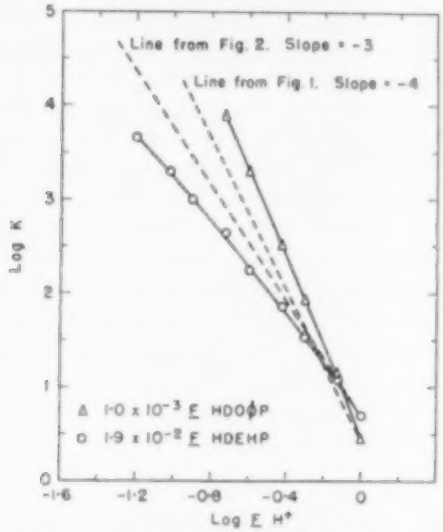

FIG. 5.—Hydrogen ion dependency of the extraction of Th(IV) into HDOΦP (toluene) and HDEHP (toluene) from an aqueous $ClO_4^- + NO_3^-$ solution, $\mu = 1{\cdot}0$, in which $[NO_3^-] = [H^+]$ and $[H^+] + [Na^+] = 1{\cdot}0$.

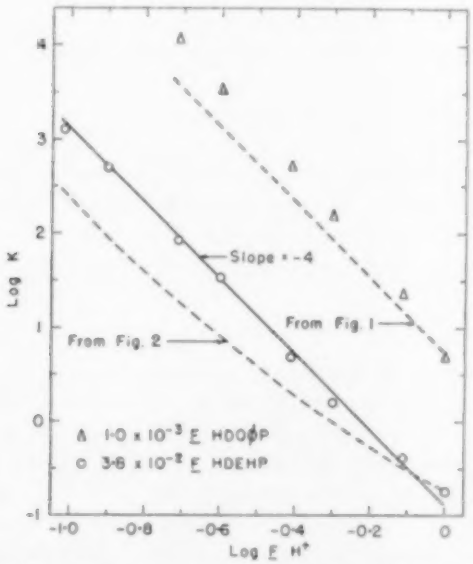

FIG. 6.—Hydrogen ion dependency of the extraction of Th(IV) into HDOΦP (toluene) and HDEHP (toluene) from an aqueous HCl solution, $[H^+] = [Cl^-]$.

curve is seen to begin with a limiting slope of —4 at low acid and become more negative as the hydrogen ion concentration (and hence chloride ion concentration) increases, in line with the expected aqueous phase chloride complexing effect and the difficult to predict effect of a varying μ.[12] The HDEHP curve is represented reasonably well by a single straight line of slope —4, the depressant effect of aqueous

phase chloride complexing, the enhancing effect of increased chloride concentration on the extraction of a chloride-containing species and the effect of a varying μ presumably mutually compensating.

The content of chloride and nitrate, respectively, in the pertinent equilibrated HDEHP phases containing gross thorium has been determined under a variety of conditions, including several different total concentrations of HDEHP and several different total HDEHP to Th ratios. In each case, after correcting for the blank, the ratio of nitrate to thorium in the extract lay within the range $1{\cdot}0 \pm 0{\cdot}2$. On the other hand, the ratio of chloride to thorium in the extract, under conditions investigated, never exceeded 0·3, the ratio decreasing with decreasing acidity as might be predicted from the tracer data. The difficulties involved in performing accurate perchlorate analyses under similar conditions have thus far rendered a corresponding study of gross perchlorate extraction impossible. It is hoped that a suitable technique may be devised and that this ion may be included in the more comprehensive investigation of gross anion effects now in progress.

Solvent dependencies

The solvent dependency, i.e. the dependency of K for Th(IV) upon the concentration of the HDGP extractant in the HDGP–toluene phase, is seen to be directly third power for 1 M $HClO_4$, 1 M HCl and 1 M HNO_3 for both HDOΦP (Fig. 7) and HDEHP (Fig. 8). This third-power dependency must be reconciled with the facts that in each of the three HDOΦP systems there is no evidence of extraction of the anion of the mineral acid while in the HDEHP the extraction of the anion varies from moderate extraction in the HCl and $HClO_4$ systems to extraction of one mole of nitrate per mole of thorium in the HNO_3 system. It should be noted that HDEHP shows a third-power dependency for 0·25 F $HClO_4$, also, Fig. 8, in which presumably no extraction of anion is involved. These dependencies are consistent with formulation of the extracted species as $Th[H(DO\Phi P)_2]_2[DO\Phi P]_2$, $Th[H(DEHP)_2]_2[DEHP]_2$ and $Th[H(DEHP)_2]_3[X]$, considering that the extractant, HDGP, is dimeric in toluene.[7,14] This interpretation is treated in greater detail in the DISCUSSION section.

GENERAL

On the basis of the previous discovery[9] of the pronounced extractions of Th(IV) by mono 2-ethylhexyl phosphoric acid, H_2MEHP, the possibility of interference due to H_2MGP present as a trace impurity in the HDGP was investigated. It was found that the K for Th(IV) from 0·5 F $HClO_4$ into 3×10^{-2} F HDEHP was increased to twice its value by making the extracting solvent also 3×10^{-6} F in H_2MEHP (100 p.p.m. contamination on the basis of formality) and was increased by a factor of approximately 500 by making the solvent 3×10^{-4} F in H_2MEHP (one per cent contamination on the basis of formality). A solvent dependency study using HDEHP one per cent contaminated with H_2MGP gave a result only slightly greater than first-power, to be compared with the third-power dependency of Fig. 8.

However, an otherwise identical study in which each solvent phase was also 0·4 F in tri-n-butyl phosphate, TBP, showed a third-power dependency, the curve being displaced downward somewhat, approximately a factor of three, from that for

[14] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).

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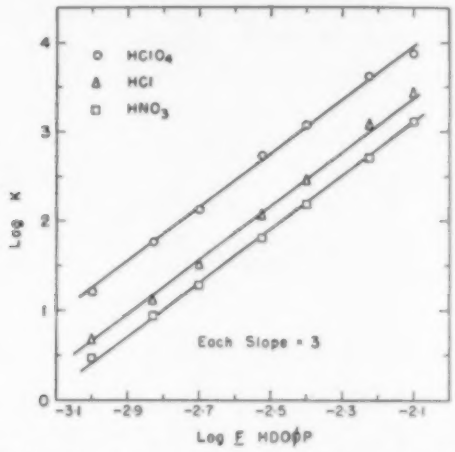

FIG. 7.—Solvent dependency of the extraction of Th(IV) into HDOΦP (toluene) from aqueous 1·0 F solutions of $HClO_4$, HCl and HNO_3.

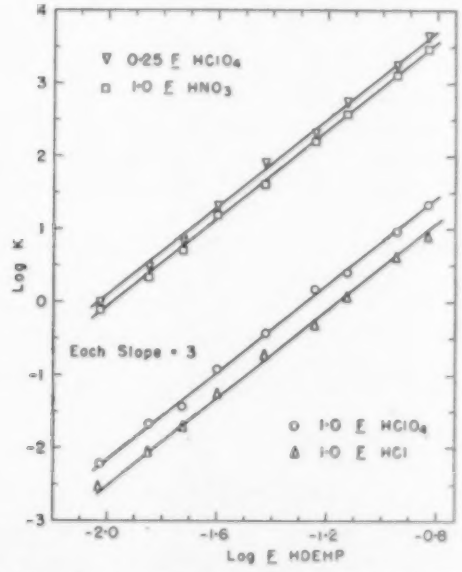

FIG. 8.—Solvent dependency of the extraction of Th(IV) into HDEHP (toluene) from aqueous 0·25 F $HClO_4$ and 1·0 F $HClO_4$, HCl and HNO_3 solutions.

the presumably pure HDEHP. It is apparent that, with respect to extraction of Th(IV), the TBP exerts an extremely strong depressant action upon the H_2MEHP (implying a strong interaction between TBP and H_2MEHP) but only a slight depressant action upon the HDEHP.

In a solvent dependency study employing the presumably pure HDEHP diluted with toluene, in which each of the solvent phases was 0·4 F in TBP, a straight line of slope 3·0, displaced by a factor of approximately three below that obtained in an otherwise identical study employing no TBP, was obtained. Similar results were

obtained in corresponding studies involving HDOΦP and $H_2MO\Phi P$. Consequently, it is concluded that neither the HDEHP nor HDOΦP employed in these studies has an interfering content of the corresponding mono ester.

DISCUSSION

Considering first the extractions in which complexing by inorganic anions in the aqueous phase is considered to produce a constant effect, a tetravalent metallic ion, such as Th(IV), may by analogy with the reported mechanism of extraction of trivalent lanthanides and actinides by HDGP[6] be considered to extract according to the following equation

$$M_A^{4+} + 4(HY)_{2_O} \rightleftharpoons M(HY_2)_{4_O} + 4H_A^+ \tag{1}$$

where M^{4+} represents the metallic ion without regard to hydration, $(HY)_2$ represents the dimeric solvent, $(HDGP)_2$, and the subscripts A and O refer to the equilibrated aqueous and organic phases respectively. The corresponding expression for the distribution ratio, K, is

$$K = k_1 \frac{[(HY)_2]_O^4}{[H^+]_A^4}$$

where k_1 is the equilibrium constant for equation (1).

However, in all of the systems presently reported the solvent dependency, i.e. dependency upon the concentration of $(HDGP)_2$ in the organic phase, is third-power, not fourth-power. Consequently, the simple reaction represented by equation (1) can not be correct.

Since thenoyltrifluoroacetone, HTTA, has been shown to form a $Th(TTA)^{3+}$ complex in an aqueous phase and since the formation of this complex must be corrected for in precise HTTA extraction studies involving Th(IV),[10,11] the corresponding possibility was considered in the HDGP extractions, as follows:

$$M_A^{4+} + (HY)_{2_O} \rightleftharpoons M(HY_2)_A^{3+} + H_A^+ \tag{2}$$

$$M(HY_2)_A^{3+} + 3(HY)_{2_O} \rightleftharpoons M(HY_2)_{4_O} + 3H_A^+ \tag{3}$$

The corresponding expression for the distribution ratio, K, is

$$K = \left(1 + k_2 \frac{[(HY)_2]_O}{[H^+]_A}\right)^{-1} \times \left(k_2 k_3 \left(\frac{[(HY)_2]_O^4}{[H^+]_A^4}\right)\right)$$

It is apparent that if $k_2[(HY)_2]_O/[H^+]_A$ is very large with respect to unity K becomes third-power solvent dependent, in accord with the data (Figs. 7 and 8), but also inverse third-power acid dependent, in contradiction of the data (Figs. 1, 2 and 3).

However, complexing of the Th(IV) by a single neutral solvent dimer in the aqueous phase to form a +4 complex rather than a +3 complex should be considered, also, as follows:

$$M_A^{4+} + (HY)_{2_O} \rightleftharpoons M(HY)_{2_A}^{4+} \tag{4}$$

$$M(HY)_{2A}^{4+} + 3(HY)_{2_O} \rightleftharpoons M(HY_2)_{4_O} + 4H_A^+ \tag{5}$$

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the corresponding expression for K being

$$K = (1 + k_4[(HY)_2]_O)^{-1} \times \left(k_4 k_5 \frac{[(HY)_2]_O{}^4}{[H^+]_A{}^4}\right)$$

If $k_4[(HY)_2]_O$ is very large with respect to unity, K becomes third-power solvent dependent while remaining inversely fourth-power acid dependent. However, in some of the studies reported the $[(HY)_2]_O$ is 5×10^{-4} M, so that k_4 is thus required to be 10^4 or greater. However, as will be seen in the discussion of nitrate complexing, k_4 must necessarily be less than 4×10^2, since in the plots of Figs. 4 and 9 the quantity

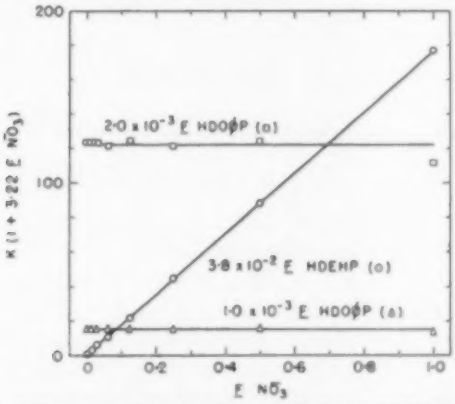

FIG. 9.—Effect of NO_3^- upon the extraction of Th(IV) into HDOΦP (toluene) and HDEHP (toluene), interpreted in terms of $Th(NO_3)^{3+}$ formation, $k = 3{\cdot}22$ (assumed). $[H^+] = 1{\cdot}0$, $\mu = 1{\cdot}0$, $HClO_4 + HNO_3$.

$(1 + 3{\cdot}22[NO_3^-])$ would need to be replaced by the quantity $\{(1 + k_2[(HY)_2]_O) + 3{\cdot}22[NO_3^-]\}$ and if the quantity $(1 + k_2[(HY)_2]_O)$ were appreciably greater than unity gross departure of the data from the plotted equations would result. Consequently, the mechanism represented by expressions (4) and (5) must be discarded as the principal mechanism.

Bearing in mind that the extract resulting from saturating a $(HDGP)_2$ solvent phase with Th(IV) by successive contacts with portions of an aqueous phase containing a gross concentration of essentially neutral thorium chloride contains a species of empirical formula $Th(DGP)_4$[13] it may be postulated that the extraction of tracer-level Th(IV) by $(HDGP)_2$ in large excess involves both monomers and dimers in the extracted species.

Such an extraction may be represented as

$$M_A{}^{4+} + 3(HY)_{2_O} \rightleftharpoons MY_2(HY_2)_{2_O} + 4H_A{}^+ \qquad (6)$$

the corresponding expression for K being

$$K_6 = k_6 \frac{[(HY)_2]_O{}^3}{[H^+]_A{}^4}$$

This expression is seen to be consistent with all of the solvent dependency data of Figs. 7 and 8, with the acid dependency data of Fig. 1 and with the acid dependency data, in the low-acid range, of Figs. 2 and 3 except for the nitrate data.

From the known tendency of Th^{4+} to form complexes with inorganic anions[10–12] in an aqueous phase the following reaction must also be considered (ignoring additional complexes).

$$M_A^{4+} + X_A^- \rightleftharpoons MX_A^{3+} \tag{7}$$

and from the established extraction[13] of Th(IV) as $Th(NO_3)(DGP)_3$ the following general reaction should be added:

$$MX_A^{3+} + 3(HY)_{2_O} \rightleftharpoons MX(HY_2)_{3_O} + 3H_A^+ \tag{8}$$

Considering reactions (6), (7) and (8) as representing co-existing equilibria the expression for K is:

$$K = (1 + k_7[X^-])^{-1}\left\{k_6\frac{[(HY)_2]_O^3}{[H^+]_A^4} + k_7k_8\frac{[(HY)_2]^3}{[H^+]^3}[X^-]\right\} \tag{9}$$

which by substitution of K_6 and K_8 for their equivalent quantities is transformed into

$$K = (1 + k_7[X^-])^{-1}(K_6 + K_8k_7[X^-]) \tag{10}$$

Consequently a plot of $K(1 + k_7[X^-])$ vs. $[X^-]$ permits evaluation of K_6 and K_8 and hence of k_6 and k_8. Such a plot has been made in Fig. 9, where X^- is NO_3^-.

The value to be used for k_7 (at $\mu = 1{\cdot}0$) was obtained by transforming the value given by DAY and STOUGHTON[11] (at $\mu = 0{\cdot}5$) by assuming the same ratios as reported by WAGGENER and STOUGHTON[12] in the corresponding k values of the first chloride complex at $\mu = 1{\cdot}0$ and $\mu = 0{\cdot}5$. This derived value of 3·22 (cf. 4·73 at $\mu = 0{\cdot}5$),[11] while not definitive, is considered valid for the present purposes.

It is to be noted from Fig. 9 that the plots (at two different concentrations of solvent) for HDOΦP have zero slope indicating a value of zero for K_8, i.e. negligible extraction of a nitrate-containing species. The HDEHP data, however, fit a line of strong positive slope indicating a value of K_8 of 55 from which k_8 is calculated to be $8{\cdot}0 \times 10^6$. From the corresponding K_1 value of 0·30, k_6 is calculated to be $4{\cdot}5 \times 10^4$. The K_6 value for the HDOΦP systems of Fig. 9 leads to a value of $1{\cdot}2 \times 10^{11}$ for k_6 in the HDOΦP system. Consequently equation 9 reduces to the following for the HDOΦP and HDEHP extraction systems at $\mu = 1{\cdot}0$ where the anions are NO_3^- and ClO_4^-:

$$K = (1 + 3{\cdot}22[NO_3^-])^{-1}\left\{1{\cdot}2 \times 10^{11}\frac{[(HDO\Phi P)_2]_O^3}{[H^+]_A^4}\right\} \tag{11}$$

$$K = (1 + 3{\cdot}22[NO_3^-])^{-1}\left\{4{\cdot}5 \times 10^4\frac{[(HDEHP)_2]_O^3}{[H^+]_A^4} + 2{\cdot}7 \times 10^7\frac{[(HDEHP)_2]_O^3}{[H^+]_A^3}[NO_3^-]_A\right\} \tag{12}$$

Equations 11 and 12 also reduce to the K expressions for the corresponding perchlorate systems if zero is substituted for $[NO_3^-]$. It is apparent from equation 12 that appreciable departure from an inverse third-power acid dependency is to be expected only at low $[NO_3^-]$ and/or low $[H^+]$. Both equation 11 and equation 12 agree with the data of Fig. 5 very well.

The same equations are shown to be in agreement with the data of Fig. 4. In this plot the effect of replacing ClO_4^- ion by NO_3^- ion, at $\mu = 1$, $[H^+] = 1$, is shown to

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enhance the K in the HDEHP system and depress the K in the HDOΦP system in accordance with aqueous phase complexing of the Th(IV) and extraction of the complex into HDEHP and non-extraction of the complex into HDOΦP.

By similar reasoning a modification of equation 9 may be used to interpret the chloride and perchlorate data of Figs. 2, 3, 6, 7 and 8. At $\mu = 1{\cdot}0$, only the complex $ThCl^{3+}$ is assumed, but at $\mu = 4{\cdot}0$ (Fig. 3) the four complexes must be considered.[12] In equation 9, if k_8 is sufficiently small, K should be inversely fourth-power acid dependent at low acidity, but the dependency should approach inverse third-power at sufficiently high acidity. (This acidity, of course, may be unattainable.) Likewise, the slope should depart from -4 in the direction of -3 more and more as the concentration of chloride ion is increased. These conclusions are qualitatively consistent with the data of Figs. 2 and 3. It should be noted that this interpretation requires that ClO_4^- ion as well as Cl^- ion enter into the extracted species in the HDEHP systems (Fig. 2). There is no evidence of such extraction in the HDOΦP system (Fig. 1).

Using the values of the stability constants of WAGGENER and STOUGHTON[12] for the first four chloride complexes of Th(IV) at $\mu = 1{\cdot}0$ and $\mu = 4{\cdot}0$ it may be calculated, on the two assumptions of no extraction of chloride-containing species and no general depressant μ effect, that the curves of Fig. 3 should differ in placement by a factor of 7·7. The experimental factor of approximately eighteen in the low-acid region indicates a depressant μ effect which is being studied in detail. This factor is seen to decrease with increasing acidity indicating greater relative extraction of a chloride-containing species at high acid from 4 M Cl^- than from 1 M Cl^-.

It should be noted, further, that the spacing between the $HClO_4$ and HCl curves (Figs. 1, 7 and 8) and between the $HClO_4$ and HNO_3 curves (Figs. 1 and 7) are respectively factors of 3·5 (ClO_4^-–Cl^-) and 4·8 (ClO_4^-–NO_3^-) to be compared with 2·5 (ClO_4^-–Cl^-) calculated from the values of WAGGENER and STOUGHTON[12] and 4·2 (ClO_4^-–NO_3^-) calculated on the assumption of $k = 3{\cdot}22$ for the stability constant of $Th(NO_3)^{3+}$, at $\mu = 1{\cdot}0$, see discussion following equation 10. In this connection it is interesting to note that the data plotted in Fig. 3 of the WAGGENER and STOUGHTON[12] study indicate a factor of approximately 3·4 (rather than 2·5) for the (ClO_4^-–Cl^-) difference. This disparity probably indicates the importance of chloride complexes beyond the first, even at $\mu = 1$.

In recapitulation, it is concluded that reactions represented by equations (6), (7) and (8) are all involved in extraction of Th^{4+}, by $(HDGP)_2$ and that equation (9) or equation (10) may be used to represent K in terms of the factors involved. Whether an anion-containing species is extracted is dependent upon the nature of the anion, the nature of G, the concentration of $(HDGP)_2$ in the solvent phase and the acidity of the aqueous phase.

It is concluded that HDOΦP extracts Th(IV) exclusively by the reaction

$$Th^{4+} + 3(HDO\Phi P)_2 \rightleftharpoons Th(DO\Phi P)_2[H(DO\Phi P)_2]_2 + 4H^+$$

from aqueous phases containing ClO_4^-, Cl^- or NO_3^-. This solvent thus appears eminently well suited for determining the complexity constant of various ThX^{3+}, ThX_2^{2+} etc. complexes and is being investigated with this application in mind. It is concluded, further, that in HDEHP–$HClO_4$ systems, the extracted species, under

some conditions, contains perchlorate groups. Consequently, the question of $Th(ClO_4)_a^{(4-a)+}$ complexes will be examined.

Whether the thorium is associated with the $H(DGP)_2^-$, and DGP^-, entities by ion pair association or by true co-ordination and, if the latter, by chelation or single-point attachment has not been established definitely. Further, if the extracted entity is a true co-ordination compound, the question of the co-ordination number displayed by the thorium, six or eight, remains unresolved. It is suggested, tentatively, that the extracted entity is a true co-ordination compound and that the complex containing no X is chelated to two $H(DGP)_2^-$ groups and single-point co-ordinated to two DGP^- groups while the complex containing an X group is chelated to two $H(DGP)_2^-$ groups and single-point co-ordinated to one $H(DGP)_2^-$ and one X^- group, each of the complexes thus displaying a co-ordination number of six for thorium.

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THE EFFECTS OF ALTERING ALKYL SUBSTITUENTS IN TRIALKYL PHOSPHATES ON THE EXTRACTION OF ACTINIDES*

T. H. SIDDALL, III
E.I. du Pont de Nemours & Co., Savannah River Laboratory
Aiken, South Carolina

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Abstract—The extraction of neptunium(VI), plutonium(VI), neptunium(IV) and plutonium(IV) nitrates by trialkyl phosphates follows the same general pattern as the extraction of uranyl nitrate when the alkyl groups are varied. However, the extraction of thorium nitrate is greatly depressed when bulky alkyl groups are introduced into the extractant molecule. This behaviour of thorium nitrate appears to be due to the fact that three extractant molecules are co-ordinated to each thorium atom in the prevalent mode of extraction. Only two molecules of extractant are required for the other actinides.

IN another paper[1] the writer has described the effects on the extraction of uranyl nitrate of altering the substituents in esters of the acids of phosphorus. This work has been continued in order to examine the effects of these substituents on the extraction of tracer concentrations of thorium, neptunium(IV), neptunium(VI), plutonium(IV) and plutonium(VI) nitrates.

MATERIALS AND EXPERIMENTAL TECHNIQUES

The extractants were prepared by the reaction of the appropriate alcohol with $POCl_3$ in the presence of pyridine or obtained as samples as indicated in Table 1. The extractants were purified either by crystallizing the addition compound with uranyl nitrate or by molecular distillation. All extractant solutions were washed with 1 M sodium hydroxide, water and nitric acid immediately before use. The n-dodecane was obtained from the Humphrey–Wilkinson Company and was passed through a column packed with Linde's 13X molecular sieve.

The desired oxidation states of neptunium and plutonium were obtained by heating with ferrous sulphamate, sodium nitrite, or ceric ammonium nitrate as was appropriate. These reagents were also used as holding oxidants or reductants as indicated in Table 1. When these reagents were used, the aqueous phase from the first agitation with the extractant phase was discarded. The extractant phase was then agitated with a fresh sample of aqueous phase and the two phases sampled in duplicate for radiometric determinations. The two phases were agitated for 2 min by use of syringe and transfer pipette, and then centrifuged before sampling. ^{234}Th, ^{233}U, ^{237}Np and ^{239}Pu, and ^{95}Zr were used as tracers.

RESULTS AND DISCUSSION

Extraction coefficients (concentration in the organic phase divided by concentration in the aqueous phase) for Th, Np(IV), Pu(IV), U(VI), Np(VI) and Pu(VI) with several trialkyl phosphates are given in Table 1. Except for thorium, the behaviour of the other actinides parallels the behaviour of U(VI) as the n-butyl radical is replaced by

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[1] T. H. SIDDALL, III, *J. Amer. Chem. Soc.* **81**, 4176 (1959).

other radicals. When the oxygen of the alkoxy group is linked to a secondary carbon atom, extraction generally improves. However, in this case the extraction coefficients for Th are markedly decreased.

The data in Fig. 1 show that unusually small extraction coefficients for Th with tris(4-methyl-2-amyl) phosphate are obtained over a range of concentrations of nitric acid. Thorium is actually less well extracted than zirconium throughout the range.

The data in Fig. 2 show that the small extraction coefficients observed with tracer

TABLE 1.—EXTRACTION OF QUADRIVALENT AND HEXAVALENT ACTINIDES[a] BY VARIOUS TRIALKYL PHOSPHATES AT 30°C

Trialkyl phosphate 1·09 M in n-dodecane (30% TBP is 1·09 M)	Extraction coefficients, organic/aqueous, 3·0 M nitric acid					
	Th	Np(IV)[b]	Pu(IV)[c]	U(VI)	Np(VI)[d]	Pu(VI)[d]
n-butyl[e] (TBP)	2·9	3·2	16·1	26	15·6	3·5
isobutyl[e]	2·4	2·7	11·8	22	15·9	3·4
n-amyl[e]	2·9	4·2	15·6	32	19·3	4·1
iso-amyl[f]	4·2	4·7	17·8	34	18·9	4·4
n-hexyl[e]	3·0	3·6	15·6	38	20·0	4·5
n-octyl[f]	2·4	3·4	15·3	33	15·7	3·9
2-ethylhexyl[g]	2·5	4·3	25	58	23	5·7
2-butyl[e]	0·45	4·9	28	42	20	4·6
3-amyl[e]	0·22	3·5	18·1	49	22	5·0
3-methyl-2-butyl[e]	0·18	3·0	24	47	25	5·4
4-methyl-2-amyl[e]	0·047	3·5	22	38	24	4·9

[a] All in tracer concentration
[b] Aqueous phase contained 0·01 M ferrous sulphamate
[c] Contained 0·01 M $NaNO_2$
[d] Contained 0·01 M ceric ammonium nitrate
[e] Prepared by $ROH + POCl_3 \xrightarrow{\text{pyridine}} [RO]_3 - P = O$
[f] Obtained from the Monsanto Chemical Company
[g] Obtained from the Victor Chemical Works

amounts of thorium in tris(4-methyl-2-amyl) phosphate are also found with high concentrations of thorium. Data for extraction by tri-n-butyl phosphate (TBP) are included for comparison. The TBP was diluted with "Ultrasene", a refined kerosene of low olefinic and aromatic content, rather than with n-dodecane. The substitution of one aliphatic diluent for another of about the same molecular weight does not affect extraction significantly.

A general explanation for the effect of substituents with the link through a secondary carbon atom may be found in the quantum mechanical calculations of MAYER.[2] These calculations indicate that there should be a sudden decrease in the availability of *f* orbitals for chemical bonding at some point in the actinide series. If this decrease occurs at or near thorium, the geometry of the chemical bonds with thorium could be quite different than that of the bonds formed with Np(IV) and Pu(IV). If this is so, the more bulky substituents might sterically interfere with the

[2] M. GOEPPERT-MAYER, *Phys. Rev.* **60**, 184 (1941).

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formation of thorium complexes, but the higher quadrivalent actinides would not be affected. Specifically, if three molecules of extractant were required for each atom in the principal mechanism of extraction of thorium, while Np(IV) and Pu(IV) required only two molecules, then the effect of bulky substituents would be expected.

The stoicheiometric requirements of thorium for extraction appear to be less straightforward than those of Np(IV) and Pu(IV) (and also the hexavalent actinides) where it has been demonstrated that two molecules of extractant are required for each

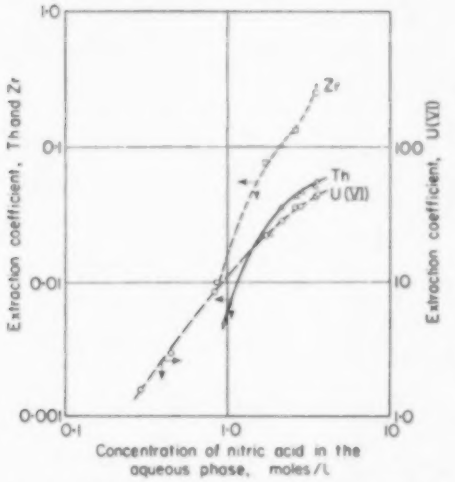

FIG. 1.—Extraction by 1·09 M tris(4-methyl-2-amyl) phosphate, 30°C.

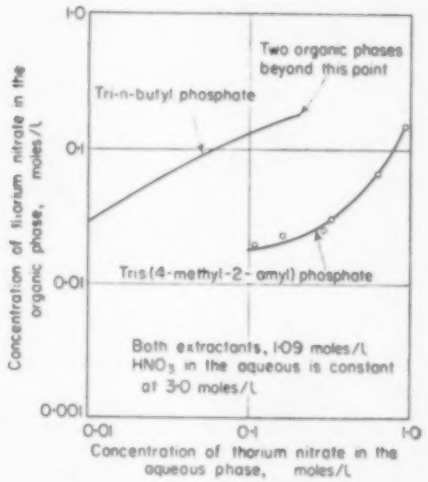

FIG. 2.—Extraction of high concentrations of thorium nitrate.

actinide atom. McKAY and his associates[3] have data that indicate that the limiting mechanism for the extraction of thorium nitrate at high dilution of extractant involves only two extractant molecules. On the other hand KATZIN[4] and the writer[5] have data to indicate that three molecules of extractant are involved in a competitive, or even principal, extraction mechanism in other than the limiting case.

The data given in Fig. 3 show that there must be a substantial difference between the stoicheiometry of the extraction of thorium and neptunium(IV) nitrates. Concentrations of extractant were varied by dilution with n-dodecane while other variables were held constant. At 1·0 molar extractant the extraction coefficients of the two quadrivalent actinides are nearly the same. At 0·06 molar extractant the extraction coefficient for thorium is a factor of about five smaller than it is for Np(IV).

The data given in Table 2 also indicate that the extraction mechanism for thorium may be different from that of Np(IV). Tri-isobutyl phosphate and tri-2-butyl phosphate were mixed in various ratios without a diluent. Other variables were kept constant and the extraction coefficients for Th and Np(IV) with 3·0 M HNO_3 in the aqueous phase were determined as a function of the ratios of the two isomers. The organic phase was titrated for nitric acid. The concentration of uncomplexed extractants was calculated by subtracting the concentration of nitric acid from total

[3] E. HESFORD, H. A. C. McKAY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
[4] L. I. KATZIN, *J. Inorg. Nucl. Chem.* **4**, 187 (1957).
[5] T. H. SIDDALL, III, *Industr. Engng. Chem.* **51**, 41 (1959).

extractant concentrations. Each extractant was assumed to extract nitric acid in proportion to its mole ratio (mole ratio × the concentration of acid extracted by pure isomer).

In such experiments, if one assumes that only two molecules of extractant are

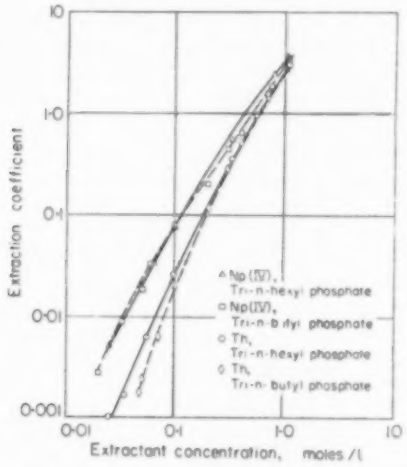

FIG. 3.—Extraction of Th and Np(IV) as a function of extractant concentration, 3·0 M HNO_3, 30°C.

TABLE 2.—EXTRACTION BY MIXTURES OF TRI-ISOBUTYL PHOSPHATE AND TRI-2-BUTYL PHOSPHATE, 3·0 M HNO_3, 30°C

Weight % tri-2-butyl phosphate	Concentration of HNO_3 in organic phase, (M/l.)	Concentration of uncomplexed tri-2-butyl phosphate, (M/l.) x	Concentration of uncomplexed tri-isobutyl phosphate, (M/l.) y	Extraction coefficient, Th	Extraction coefficient, Np(IV)	$\frac{E-E_1x^2-E_3y^2}{xy}$, Th	$\frac{E-E_1x^2-E_3y^2}{xy}$, Np(IV)
100	2·09	1·21	0	3·27	30·3	—	—
80	2·07	0·97	0·266	4·36	28·0	6·2	30
60	2·06	0·73	0·53	8·2	26·0	11·4	30
40	2·04	0·48	0·80	12·9	24·0	16·8	30
20	2·01	0·242	1·06	15·4	23·0	19·5	34
10	—	0·121	1·20	16·5	—	23	—
5	—	0·061	1·26	16·5	—	25	—
0	1·97	0	1·33	16·2	20·9	—	—

involved in the extraction mechanism, the measured extraction coefficient should obey the relation:

$$E = E_1x^2 + E_2xy + E_3y^2 \qquad (1)$$

where x is the concentration of that part of one extractant that is uncomplexed by nitric acid, y is the concentration of the other, and E_1, E_2 and E_3 are the extraction coefficients that would be obtained when the concentration of uncomplexed extractant is 1·0 molar. E_1 and E_3 can be calculated from the extraction coefficients that are obtained with the unmixed extractants. In that case,

$$\frac{E - E_1x^2 - E_3y^2}{xy} = E_2 \qquad \text{which is a constant.} \qquad (2)$$

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The data in Table 2 show that the calculated values of E_2 are constant for Np(IV) as expected. The values of E_2 for Th are not constant and even show a definite trend. Similar but cruder experiments with mixtures of tri-3-amyl phosphate and tri-n-amyl phosphate showed the same effect for thorium. However, with mixtures of tri-2-butyl phosphate and TBP the calculated values of E_2 were constant, within experimental error, for thorium as well as for Np(IV).

It is not felt that these experiments with mixtures of isomers conclusively demonstrate that thorium nitrate requires more extractant molecules than Np(IV), but that they have increased the probability that this is so. When three molecules of extractant are involved, the equation is:

$$E = E_1x^3 + E_2x^2y + E_3xy^2 + E_4y^3 \tag{3}$$

With so many constants involved, equation (3) could, depending on the true values of the constants, appear to be the same as equation (1) within experimental error. Long experience has shown that the standard error in the experimental extraction coefficients is about 3 per cent. When these things are considered, the proper viewpoint is that conformance with equation (1) may be a necessary condition, but is not a sufficient condition for proof of the two-molecule mechanism.

Finally, it is not felt that the evidence and discussion given in this paper in any way conflict with the view that the limiting mechanism at small concentrations of extractant involves only two molecules for each thorium atom. The mechanism with three extractant molecules must become unimportant as the extractant is taken to high dilution. It is also possible that some factor in addition to steric hindrance contributes to make the extraction of thorium small in the cases noted. Experiments based on something more sophisticated than distribution studies with tracer thorium are needed to test such a possibility.

Whatever the cause of the effects noted for thorium, it is evident that esters with bulky substituents may be of practical value. Uranium and thorium ores are often found together. The separation of thorium from uranium and also from other actinides should be greatly improved by substituting such an extractant as tris(4-methyl-2-amyl) phosphate for TBP. While tris(4-methyl-2-amyl) phosphate is not commercially available, within the writer's knowledge, 4-methyl-2-pentanol (methyl isobutyl carbinol) and other secondary alcohols are available. The corresponding trialkyl phosphates can be readily synthesized.

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THE EXTRACTION OF MINERAL ACIDS BY TRI-n-BUTYL PHOSPHATE (TBP)

E. HESFORD and H. A. C. MCKAY
Atomic Energy Research Establishment, Harwell, Didcot, Berks

(*Received* 29 *August* 1959)

Abstract—The physical chemistry of the extraction of HCl, HNO_3, H_2SO_4, $HClO_4$ and HF from aqueous solution by tri-n-butyl phosphate (TBP) has been studied. Electrical conductivity and viscosity measurements show that $HClO_4$ is a strong electrolyte in TBP, but that the other acids only ionize to a limited extent; the ionization constants of HCl, HNO_3 and H_2SO_4 (first dissociation) are all equal to about 9×10^{-5}. The partition results are in accord with these conclusions, and indicate also the formation of HCl·TBP, HNO_3·TBP, H_2SO_4·TBP, and $HClO_4$·TBP; perchloric acid appears moreover to yield higher solvates in addition to the mono-solvate. The water content of the TBP phase increases with acid concentration in all cases except that of HNO_3, and this may help to explain certain differences in viscosity and conductivity which appear at high acidities.

ALCOCK *et al.*[1] have made a detailed study of the extraction of HNO_3 by tri-n-butyl phosphate (TBP), and other authors, especially BALDWIN *et al.*,[2] have examined the corresponding HCl system, while POVITSKY *et al.*,[3] have investigated the extraction of $HClO_4$. The present paper contains new results for all these systems, and in addition for those involving H_2SO_4 and HF.

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METHODS AND RESULTS

Materials and solutions. The TBP was purified by the usual method,[1] and the acids were all of A.R. grade. The TBP solutions studied were generally obtained by equilibration with an aqueous phase, and consequently contained the equilibrium amount of water. The equilibrations were carried out by stirring in centrifuge tubes for at least 10 min in a thermostat at 25°C; a few checks were made to confirm that this is a sufficient time. All the measurements mentioned below were also made at 25°C.

Viscosity. Viscosities were determined with an Ostwald viscometer. The results are plotted in Fig. 1.

Electrical conductivity. The conductivity measurements were generally made with a Mullard bridge at 2900 c/s, using "black" platinum electrodes. Some checks were also made at 1000 c/s and using bright platinum electrodes, but these changes did not affect the readings by more than a few per cent. The results have been combined with the viscosities and plotted in Fig. 2 as $\Lambda\eta/30$ (Λ = molar conductivity, η = viscosity), which should be an approximate measure of the degree of ionization (see Discussion below).

The conductivity data for HNO_3 are roughly ten times as high as those given by ALCOCK *et al.*[1] This seems to be due to an error in reading the instrument in the earlier paper. The revised estimates of the degree of ionization are high enough to have an appreciable effect on the deviation of the partition data from ideality, but not to affect the general conclusions drawn by ALCOCK *et al.*

Water content. The water content of the TBP phase was determined in all cases by Karl Fischer titration. The results are given in Fig. 3, those for HNO_3 being taken from ALCOCK *et al.*[1] Our HCl results agree with those of BALDWIN *et al.*[2]

Partition measurements. The partition results were based on titrations of the two phases after equilibration as described above. At low acidities the titrations were carried out with N/100 NaOH to pH

[1] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[2] W. H. BALDWIN, C. E. HIGGINS and B. A. SOLDANO, *J. Phys. Chem.* **63**, 118 (1959); see also H. IRVING and D. N. EDGINGTON *J. Inorg. Nucl. Chem.* **10**, 306 (1959).
[3] N. S. POVITSKY, A. S. SOLOVKIN and I. V. SHILIN, *Zh. Neorg. Khim.* **3**, 222 (1958).

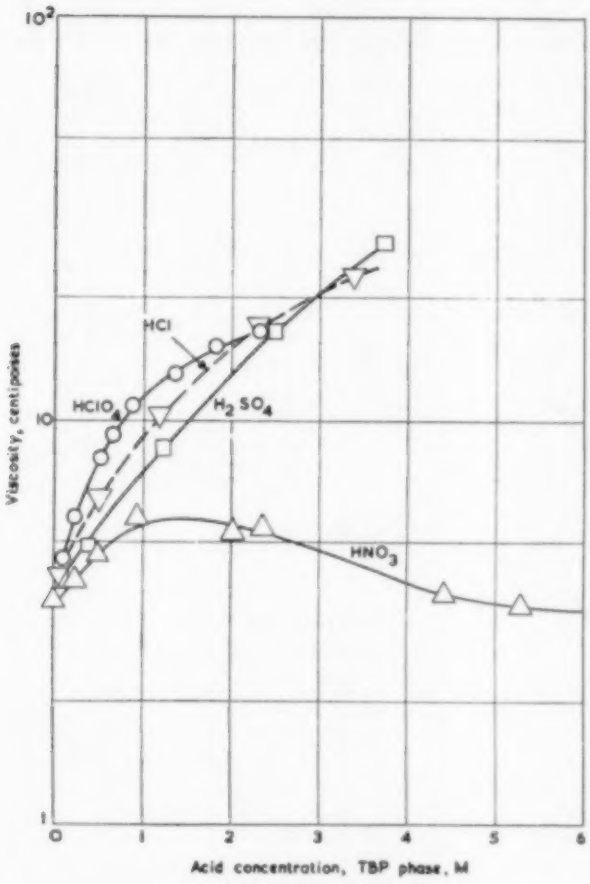

FIG. 1.—Viscosity of TBP phase.

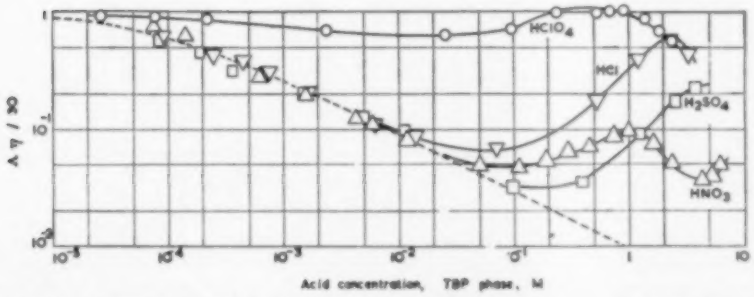

FIG. 2.—Estimated degree of ionization ($\Lambda\eta/30$) of acids in TBP phase. The dashed curve is a theoretical curve based on the Ostwald dilution law, assuming a dissociation constant of 9×10^{-5}.

7 using a pH meter. At high acidities N/10 NaOH and an indicator were used. The results for 100% TBP are given in Fig. 4, and again in Fig. 5 where the aqueous phase activity is plotted in place of the molarity. Activity plots only are given for the experiments using TBP in a diluent (Figs. 6 and 7).

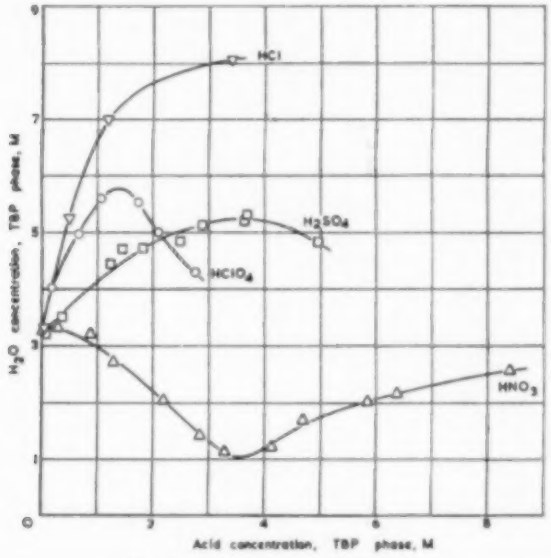

FIG. 3.—Water content of TBP phase.

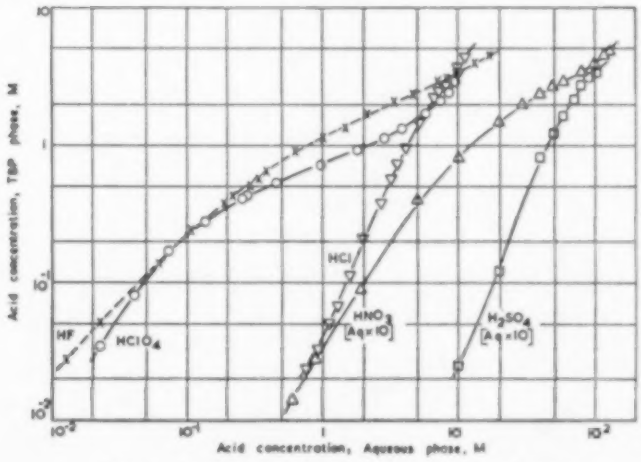

FIG. 4.—Partition of acids between 100% TBP and water.

For HCl[2,4] and HNO_3[1,4,5] there are now several sets of measurements, all in good agreement, though none extend to the very low acidities studied in the present paper. For $HClO_4$ the only results available for comparison[3] agree reasonably with ours, though again they do not cover very low acidities.

[1] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, G. W. MASON, *J. Inorg. Nucl. Chem.* **3**, 215 (1956).
[2] A. A. FOOS, H. A. WILHELM, ISC-695 (1956); D. G. TUCK, *J. Chem. Soc.* 2783 (1958); D. DYRSSEN, Private communication (1955).

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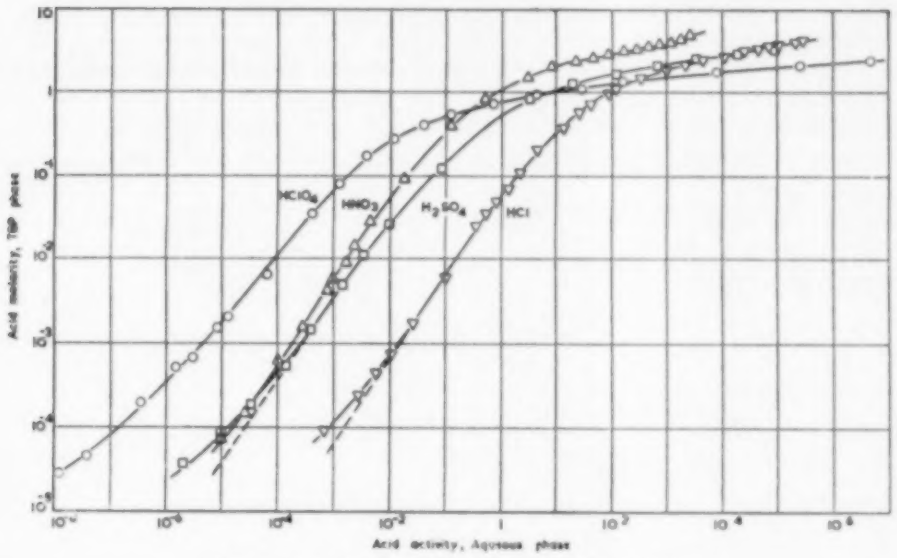

FIG. 5.—Partition of acids between 100% TBP and water.

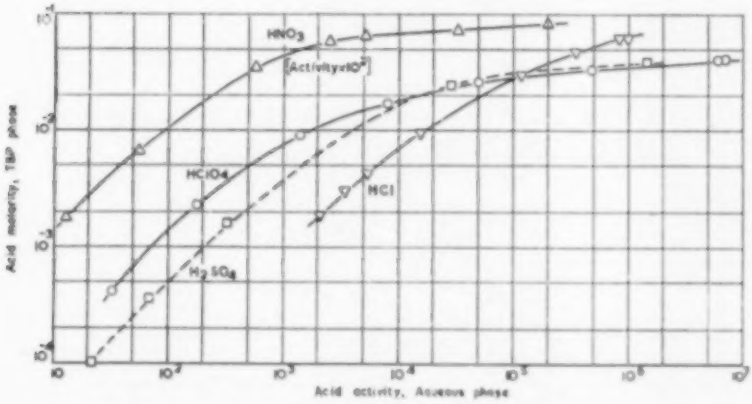

FIG. 6.—Partition of acids between 2% TBP in kerosene or benzene and water.

DISCUSSION

Ionization in the TBP *phase*

Perchloric acid. A Kohlrausch plot of the conductivity data for $HClO_4$ (Fig. 8) suggests that this acid may be virtually completely dissociated below 10^{-2} M in TBP. Fig. 8 is certainly consistent with this interpretation, assuming $\Lambda_0 = 8{\cdot}0$ (Λ_0 = molar conductivity at infinite dilution) and a dielectric constant of thirteen for wet TBP (which agrees with a previous rough estimate[6] of fourteen for the latter quantity).

The value $\Lambda_0 = 8{\cdot}0$ yields $\Lambda_0\eta_0 = 29$ for perchloric acid in TBP at infinite

[6] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).

dilution. This quantity is so low as to exclude a proton-jump mechanism for the hydrogen ion conductivity.

The conductivity of $HClO_4$ in 4% TBP in benzene is only just detectable, and ionization is evidently negligible at this and higher dilutions of the TBP.

Other acids. On the basis of the $HClO_4$ results we have taken $\Lambda\eta/30$ as a rough measure of the degree of ionization of other acids in TBP. For these particular

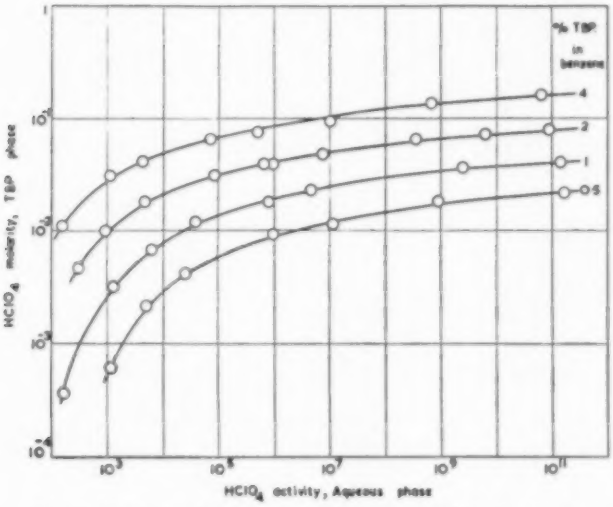

FIG. 7.—Partition of perchloric acid between TBP in benzene and water.

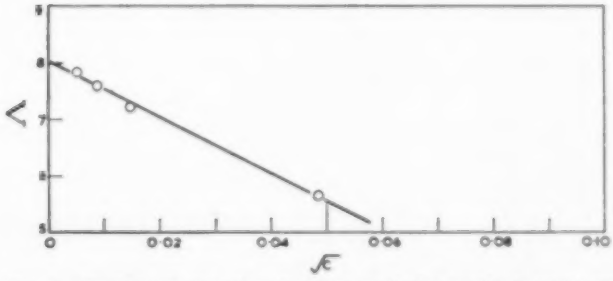

FIG. 8.—Kohlrausch plot of conductivity results for perchloric acid in TBP.

systems, this quantity is to be preferred to the expression $\Lambda\eta/60$ used previously in this laboratory[7] as it is based on immediately relevant experiments. Fig. 2 gives plots of $\Lambda\eta/30$. The molar rather than the equivalent conductivity has been used for sulphuric acid, because we are presumably dealing with single stage ionization; the second dissociation of H_2SO_4 is relatively weak and is suppressed by the hydrogen ion resulting from the strong first dissociation, so that H_2SO_4 behaves essentially as a 1 : 1-electrolyte consisting of H^+ and HSO_4^-. It is apparent from the diagram that HCl, HNO_3 and H_2SO_4 are weak acids of very similar strength in TBP, and differ sharply from $HClO_4$. The Ostwald dilution law indeed explains the results very well,

[7] H. A. C. MCKAY and A. R. MATHIESON, *Trans. Faraday Soc.* **47**, 428 (1951).

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and leads to an ionization constant of 9×10^{-5} for all three acids. The conductivity data for HF (not quoted) show that this acid is much weaker still. Above about 0·1 M the Ostwald law fails, and there is a rise in ionization with concentration for HCl, HNO_3 and H_2SO_4. This self-ionizing effect has already been noted for HNO_3, and is common in solvents of low dielectric constant. All these acids are negligibly ionized in 2% TBP in diluent.

The water content of the TBP *phase*

Perhaps the most interesting feature of the hydration measurements in Fig. 3 is the contrast between HNO_3 and the other acids studied. ZALDWIN *et al.*[2] have already remarked on the difference between HNO_3 and HCL, and we have now found a similar, though smaller difference between HNO_3, and H_2SO_4 or $HClO_4$.

The difference in water content of the TBP phases may be the cause of certain other differences observed at relatively high acid concentrations. These include:

(1) *Viscosity*. It may be suggested that water molecules, with their powerful external fields, tend to restrict free flow, and hence tend to increase the viscosity. This would explain why the viscosities of the HCl, H_2SO_4 and $HClO_4$ solutions continue to rise with concentration, whereas that of HNO_3 varies very little (Fig. 1).

(2) *Degree of ionization*. Above 1 M, HNO_3 apparently ionizes much less than HCl or H_2SO_4 (Fig. 2). This again is in the direction to be expected, since water molecules would tend to raise the dielectric constant of the medium.

Extraction by 100% TBP

Hydrochloric and nitric acids. There is a region where ionization of HCl and HNO_3 in the TBP phase is, to a first approximation, negligible. In this region the partition law may be written

$$a = Cy = Ka' = K(C'y')^2 \tag{1}$$

(a = activity, C = concentration, y = molar activity coefficient, K = constant, prime $'$ denotes aqueous phase). Moreover below about $C = 0{\cdot}1$ M the TBP phase should be an ideal solution, with $y = 1$ and

$$C = Ka' \tag{2}$$

In Fig. 5, C, the molarity of the acid in the TBP, is plotted against a', the activity in the aqueous phase. It will be seen that (2) is obeyed for both HCl and HNO_3 from about 5×10^{-4} to 5×10^{-2} M. For HCl, $K = 6{\cdot}3 \times 10^{-2}$, and for HNO_3, $K = 5{\cdot}3$.

Below 5×10^{-4} M, both acids are rather more extractable than the ideal law would indicate. This may be explained in terms of ionization in the TBP phase. Indeed if we plot the concentration of unionized acid, $(1 - \alpha)C$, instead of the total concentration, we again obtain the ideal law (dashed curves in Fig. 5).

Above 5×10^{-2} M the TBP phase can no longer be treated as ideal. With the aid of equation (1) we can calculate y, the activity coefficient of the acid in the TBP phase, and a plot of this quantity (Fig. 9) shows that it obeys the Setchénov relation

$$\log y = kC \tag{3}$$

(k = constant) up to about 2 M. For HCl, $k = 0{\cdot}8$, and for HNO_3, $k = 0{\cdot}7$. Rather

better straight lines are obtained if molalities are used instead of molarities, and the hydration of the organic phase is taken into account.[2]

Combination of the relations just discussed yields

$$\text{For HCl: } (1-\alpha)\,C \times 10^{0{\cdot}8C} = 6{\cdot}3 \times 10^{-2}a' \tag{4}$$

$$\text{For } HNO_3\text{: } (1-\alpha)\,C \times 10^{0{\cdot}7C} = 5{\cdot}3a' \tag{5}$$

which are valid over the range 10^{-4} to 2 M.

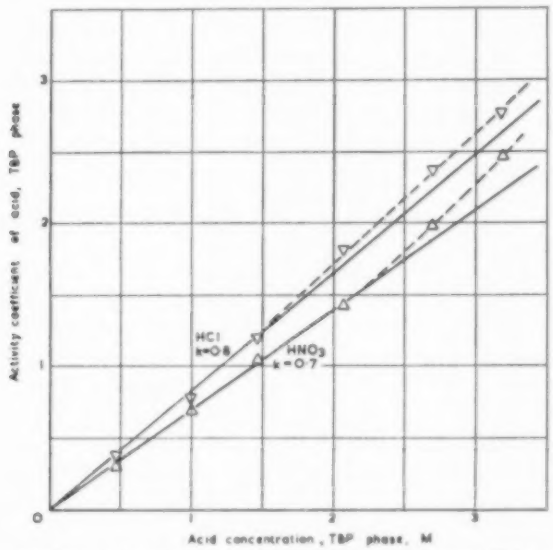

FIG. 9.—Setchénov plots of partition results for hydrochloric and nitric acids in TBP.

In the HNO_3 case, ALCOCK *et al.*[1] have shown that the principal chemical process in the extraction is the formation of a 1 : 1-compound, HNO_3·TBP (which may be hydrated). It is this process which is chiefly responsible for the flattening out of the partition curve at high concentrations, and hence for the high Setchénov coefficient. The extraction of HCl is sufficiently similar to that of HNO_3 to suggest that a 1 : 1-compound is again formed, HCl · TBP.

Sulphuric acid. In the region of negligible ionization

$$a = Cy = Ka' = 4K(C'y')^3, \tag{6}$$

and below $C = 0{\cdot}1$ M we should again expect equation (2) to hold. The curve in Fig. 5 is, however, never quite as steep as the ideal law requires, though there is a fair degree of approximation. K is equal to about 3.

Perchloric acid. At high dilutions $HClO_4$ appears to be completely ionized in TBP, so the partition law becomes

$$a = C^2y^2 = Ka' = K(C'y')^2 \tag{7}$$

At very high dilutions this simplifies to

$$C^2 = Ka' \tag{8}$$

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and an approximation to a square law is indeed observed in the neighbourhood of $C = 10^{-4}$ M. There is a noteworthy contrast here to the behaviour of HCl, HNO_3 and H_2SO_4, though these acids too would presumably give a square law if very high dilutions could be studied.

If we plot $y/\sqrt{K}\,(=\sqrt{a'}/C)$ for $HClO_4$ against $\sqrt{C}$, the first nine points fall roughly on a straight line, as required by the Debye–Hückel theory. Fig. 10 illustrates this, the line drawn corresponding to $K = 0{\cdot}055$ and a dielectric constant of twelve.

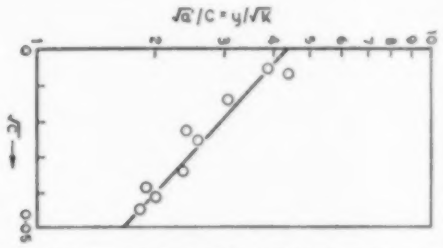

FIG. 10.—The Debye–Hückel slope of the activity coefficient plot for perchloric acid in TBP.

A continuation of the plot of $y/\sqrt{K}$ to high concentrations yields a steeply rising curve (Fig. 11) similar to those of highly solvated and highly ionized electrolytes in water, such as $HClO_4$ itself.

Hydrofluoric acid. The usual tables give no activity data for this acid in aqueous solution, so it is not possible to plot our partition results in Fig. 5. A simple concentration plot (Fig. 4) does however reveal a striking contrast between HF and HCl, HNO_3 or H_2SO_4. This may be explained by the low ionization of HF in the aqueous phase, as well as in the organic phase. Around 0·1 M there is indeed a good approximation to the original Nernst law

$$C = KC' \tag{9}$$

with $K = 2{\cdot}2$. The similarity between the HF and the $HClO_4$ curves arises because in each case the acid remains in the same state of association or dissociation during transfer between phases.

Extraction by TBP *in diluent*

Hydrochloric and nitric acids. If a dilute solution of TBP in, for example, kerosene is used as extractant it is often possible to obtain more definite information than with pure TBP, because the solutions are nearly ideal. With 1·9% TBP in kerosene (volume fraction) the formation of HNO_3·TBP has been demonstrated beyond much doubt.

Similar results with HCl again suggest the formation of HCl·TBP. It will be seen that the HCl curve in Fig. 6 runs approximately parallel to the HNO_3 curve, which has already been shown to follow the law for formation of a 1:1-compound:

$$C_{HNO_3}/(C_{TBP} - C_{HNO_3}) = 0{\cdot}16\, a'_{HNO_3} \tag{10}$$

The constant for HCl is about 10^{-3} compared with 0·16 for HNO_3.

It must be admitted, however, that the HCl curve agrees less well with theory than the HNO_3 curve, and the asymptote is less well established owing to the smaller solubility of HCl in TBP. Moreover any attempt to allow for hydration in the TBP

phase makes the HCl curve steeper rather than flatter. Further study of the HCl–TBP system is therefore desirable.

Sulphuric acid. The H_2SO_4–TBP-kerosene system readily splits into two phases, so benzene was used instead of kerosene as diluent. The results obtained (Fig. 6) unfortunately do not define any asymptote at all clearly, and at higher acidities the benzene begins to sulphonate. We think, nevertheless, than a mono-solvate may be formed, $H_2SO_4 \cdot TBP$.

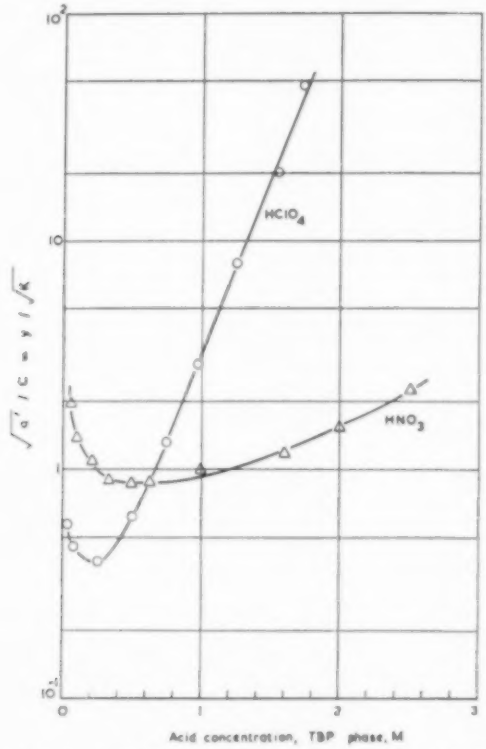

FIG. 11.—The activity coefficient of perchloric acid in TBP.

Perchloric acid. It is particularly useful to study extraction of $HClO_4$ by TBP in a diluent because ionization of the acid is suppressed by the diluent. Benzene had again to be used in place of kerosene.

The results in Fig. 7 over the range 0·5–4% TBP in benzene show a well-defined asymptote corresponding in each case to the composition $HClO_4 \cdot TBP$, and this is presumably the principal species present at high acidities. At lower acidities, however, C_{HClO_4} varies with a higher power of C_{TBP} than the first, so higher solvates must be formed. At an aqueous acidity of 5 M, for example, the law is very roughly a square law, indicating $HClO_4 \cdot 2TBP$ as a probable constituent.

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THE EXTRACTION OF URANYL PERCHLORATE BY TRI-n-BUTYL PHOSPHATE (TBP)

E. HESFORD and H. A. C. MCKAY
Atomic Energy Research Establishment, Harwell, Didcot, Berks

(*Received* 10 *June* 1959)

Abstract—$UO_2(ClO_4)_2$ differs from $UO_2(NO_3)_2$ in being appreciably ionized and hydrated in TBP. It resembles $UO_2(NO_3)_2$ in forming a di-solvate, $UO_2(ClO_4)_2 \cdot 2TBP$, at least under one set of conditions. Most features of its extraction by TBP from aqueous solutions are explicable by means of the theory that has been developed for nitrate systems, though differences in the values of the parameters lead to important differences in behaviour. Interesting and at present inadequately explained changes occur in the absorption spectrum of $UO_2(ClO_4)_2$ in TBP under different conditions.

IN the preceding paper[1] the authors have shown that $HClO_4$ differs from HNO_3 and other mineral acids in its high degree of ionization in tri-n-butyl phosphate (TBP). It seemed of interest, therefore, to study uranyl perchlorate, $UO_2(ClO_4)_2$, in comparison with uranyl nitrate. The latter is already known[2] to be very nearly unionized and unhydrated in TBP, and to be solvated with two molecules of TBP, i.e. to exist almost entirely in the form $[UO_2(NO_3)_2 \cdot 2TBP]$. $UO_2(ClO_4)_2$ proves to be substantially ionized and hydrated.

METHODS AND RESULTS

General. The experimental techniques were essentially as described in the preceding paper.[1] A Uvispek spectrophotometer was employed to determine the absorption spectra. All measurements except the spectral ones (which were at ambient temperature, ca. 22°C) were made in a thermostat at 25°C. The TBP solutions were generally water-saturated, i.e. at equilibrium with an aqueous phase.

Materials and solutions. TBP was purified by the usual method. $UO_2(ClO_4)_2$ was prepared by neutralizing UO_3 with the stoicheiometric amount of $HClO_4$ and recrystallizing from water. The TBP solutions of $UO_2(ClO_4)_2$ studied were generally water-saturated, or very nearly so, but a few experiments were also carried out on solutions which had been partially desiccated over P_2O_5.

^{233}U was employed for partition measurements at trace concentrations of uranium in presence of $HClO_4$, analysis being by α-counting.

Viscosity and electrical conductivity. The viscosity (η) results are given in Fig. 1, and the quantity $\Lambda\eta/120$ is plotted in Fig. 2 (Λ = molar conductivity). Data for $UO_2(NO_3)_2$ are given for comparison.

Water content. Fig. 3 gives the results, again with those of $UO_2(NO_3)_2$ for comparison. The latter are due to HEALY,[3] and for pure water-saturated TBP do not quite agree with ours. The discrepancy is probably due to errors in calibration of the Karl Fischer reagent.

Partition measurements. Fig. 4 gives the results of partition measurements for $UO_2(ClO_4)_2$ between water and 100% TBP. Figs. 5, 6 and 7 apply to traces of $UO_2(ClO_4)_2$ in presence of $HClO_4$. At the lowest TBP concentrations, however, the uranium concentration is no longer small in comparison with that of TBP, i.e. it is no longer strictly at trace level and corrections are necessary (see Discussion section).

Spectra. The spectrum of $UO_2(ClO_4)_2$ in TBP changes considerably according to the conditions,

[1] E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **13**, 156 (1960).
[2] T. V. HEALY and H. A. C. MCKAY, *Trans Faraday Soc.* **52**, 633 (1956).
[3] T. V. HEALY, AERE C/R 1772 (1956).

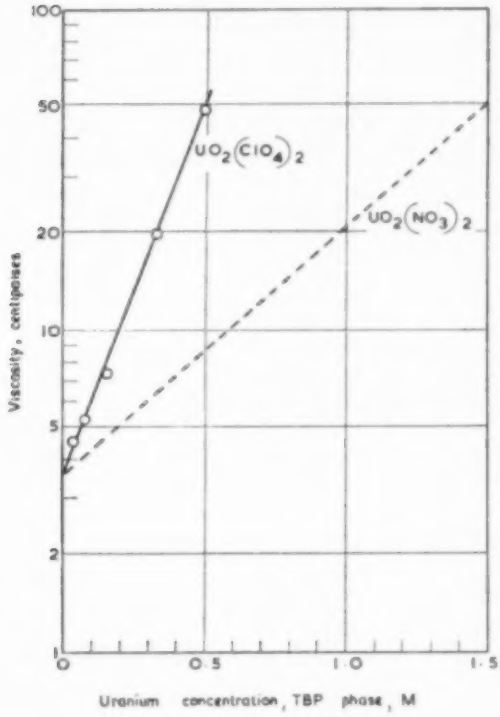

FIG. 1.—Viscosity of TBP phase
○ uranyl perchlorate, our data
– – – uranyl nitrate, HEALY.[3]

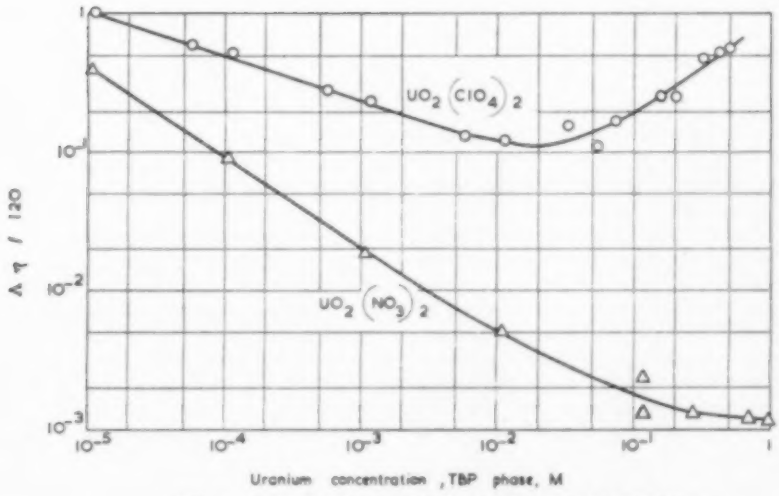

FIG. 2.—Estimated degree of ionization (see text) in TBP phase
○ uranyl perchlorate
△ uranyl nitrate.

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as shown by Figs. 8, 9 and 10. In particular the trough centred on 370 mμ often tends to "fill in", and attention has therefore been directed especially to this part of the spectrum.

DISCUSSION

Ionization in the TBP phase

For 1 : 1-electrolytes the quantity $\Lambda\eta/60$ may be used as a rough measure of the degree of ionization.[4] For 2 : 1-electrolytes the corresponding quantity would be $\Lambda\eta/120$. It is clear from Fig. 2, therefore, that $UO_2(ClO_4)_2$, unlike $UO_2(NO_3)_2$, is

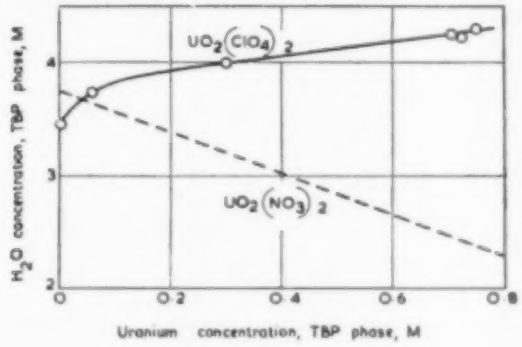

FIG. 3.—Water content of TBP phase
○ uranyl perchlorate, our data
– – – uranyl nitrate, HEALY.[3]

substantially ionized in TBP. It is difficult, however, to be sure of the precise interpretation of the results, partly because there are two stages of ionization involved and partly because $\Lambda\eta/60$ or $\Lambda\eta/120$ is at best only a rough approximation to the degree of ionization.

We take the view that $UO_2(ClO_4)_2$ is fairly completely ionized at 10^{-5} M, and that ion association occurs to a substantial extent at higher concentrations. ($\Lambda\eta$ falls more rapidly with concentration than can be explained by Debye–Hückel effects.) At 10^{-2} M, for example, as many as 80 per cent of the $UO_2(ClO_4)_2$ molecules may be unionized. Above 0·1 M there seems to be an increase in ionization again, though the significance of the quantity $\Lambda\eta$ becomes more and more doubtful as the concentration increases. $UO_2(ClO_4)_2$, it will be noted, is a weaker electrolyte than $HClO_4$ in TBP, though stronger than other mineral acids.[1]

Hydration in the TBP phase

It appears from Fig. 3 that $UO_2(ClO_4)_2$ carries a small amount of water into TBP, whereas $UO_2(NO_3)_2$ displaces water and is indeed virtually unhydrated. A possible interpretation is that free UO_2^{2+} ions are hydrated in TBP, even if unionized $[UO_2(ClO_4)_2]$, like $[UO_2(NO_3)_2]$, is unhydrated.

The TBP phase can be partially dehydrated by standing in a vacuum desiccator over phosphorus pentoxide. This causes a fall in the electrical conductivity (a factor of about three having been observed for several solutions in the range 0·1–1 M

[4] H. A. C. McKAY and A. R. MATHIESON, *Trans. Faraday Soc.* **47**, 428 (1951).

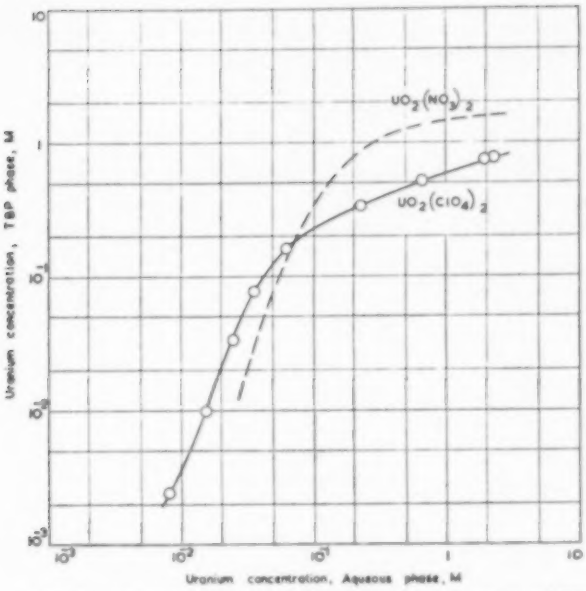

FIG. 4.—Distribution of uranyl perchlorate between water and TBP
○ uranyl perchlorate, our data
– – – uranyl nitrate, HEALY.[3]

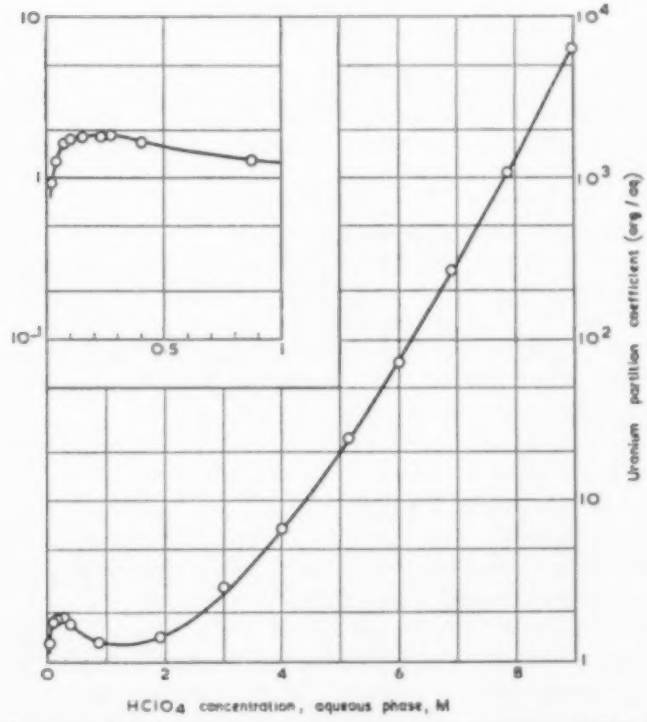

FIG. 5.—Distribution of trace amounts of uranyl perchlorate between aqueous $HClO_4$ and TBP.

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$UO_2(ClO_4)_2$). It appears therefore that ionization is suppressed by dehydration, perhaps through a reduction in the dielectric constant of the medium.

Solvation of uranyl perchlorate by TBP

There is very strong evidence[2] that $UO_2(NO_3)_2$ forms a di-solvate in TBP to the virtual exclusion of other solvates. Our results provide evidence that $UO_2(ClO_4)_2$ also forms a di-solvate, at least under one particular set of conditions. The method

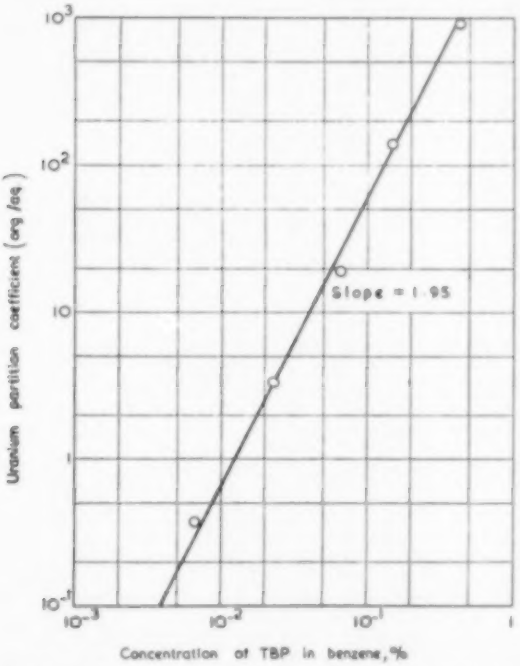

FIG. 6.—Partition coefficient as a function of TBP concentration at 10·3 M aqueous $HClO_4$.

used was one which has often been used for nitrates, viz. extraction from an aqueous phase of constant composition, at low and varying TBP concentration in diluent.[5] Provided certain conditions are fulfilled, we have

$$\text{Partition coefficient} \propto (\text{TBP concentration})^q$$

where q is the solvation number.

For extraction from aqueous $HClO_4$ solutions this method is only valid at very high $HClO_4$ concentrations, say 10–12 M. In these circumstances $HClO_4 \cdot TBP$ is formed to the virtual exclusion of higher solvates of $HClO_4$, which would otherwise bring about a failure of the simple q-power law. Fig. 6 shows that a good square-law plot is in fact obtained, indicating the formation of a di-solvate of $UO_2(ClO_4)_2$. It is important to note, however, that other solvates may be formed under other conditions, and especially at higher TBP concentrations when uranyl perchlorate is appreciably ionized.

[5] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).

Extraction of uranyl perchlorate by 100% TBP

The curves in Figs. 4 and 5 do not at present lend themselves to detailed analysis, owing to the varying and still somewhat uncertain degree of ionization of the $UO_2(ClO_4)_2$ in TBP. The following points may, however, be noted:

(1) $UO_2(ClO_4)_2$ is less extractable than $UO_2(NO_3)_2$ at high concentrations, but

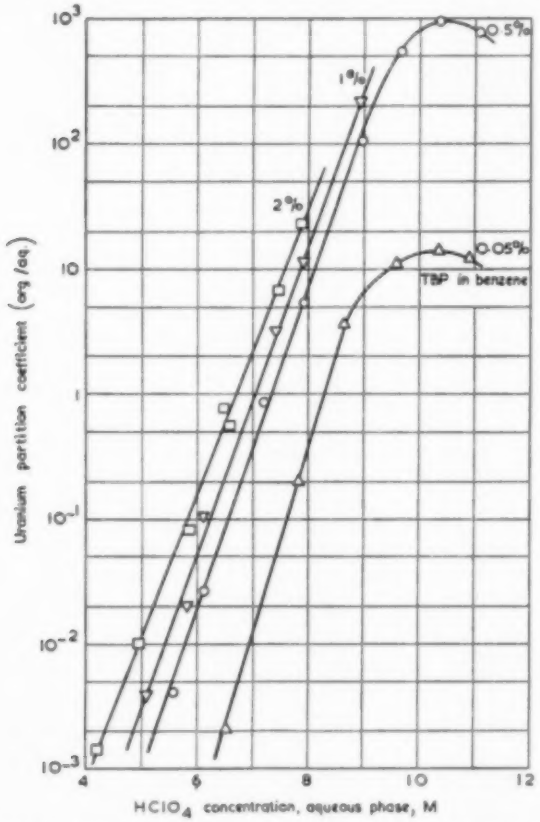

FIG. 7.—Distribution of trace amounts of uranyl perchlorate between aqueous $HClO_4$ and various concentrations of TBP in benzene.

more extractable at low concentrations. Ionization of $UO_2(ClO_4)_2$ in the TBP phase at low concentrations would give rise to just such a change in the relative extractabilities.

(2) The maximum at 0·2 M $HClO_4$ in Fig. 5 is not explicable along the lines discussed in the next section. A plausible explanation is that it arises from varying ionization of the $UO_2(ClO_4)_2$ in the TBP phase.

Extraction of traces of uranyl perchlorate by TBP *in diluent in presence of perchloric acid*

At low TBP concentrations in benzene diluent, ionization of $UO_2(ClO_4)_2$ is almost certainly negligible. We might therefore expect behaviour similar to that of $UO_2(NO_3)_2$

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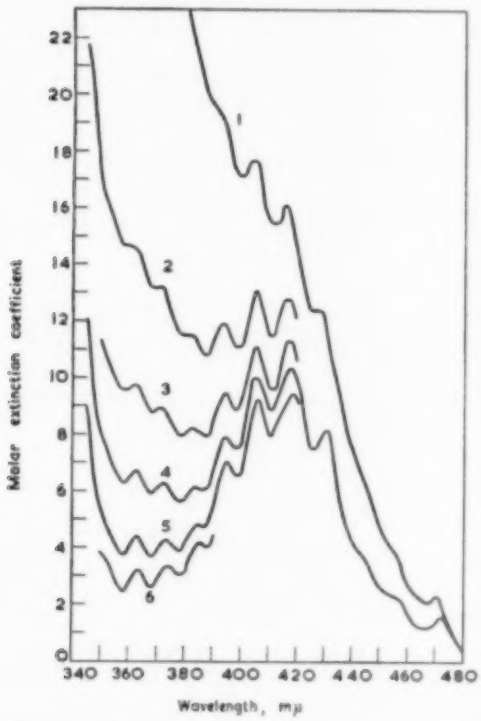

FIG. 8.—Absorption spectra of uranyl perchlorate in water-saturated TBP. U concentrations, M, 0·0024, 0·0116, 0·0226, 0·0536, 0·209, 0·441 (spectra 1–6 respect.).

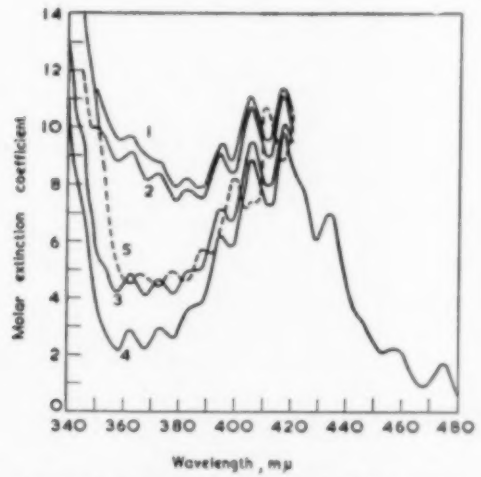

FIG. 9.—Absorption spectra of 0·0226 M uranyl perchlorate in water-saturated TBP containing $HClO_4$. $HClO_4 : UO_2(ClO_4)_2$ ratios 0 : 1, 2 : 1, 4 : 1, 7 : 1, 90 : 1 (spectra 1–5 respect.).

as discussed by HESFORD and McKAY[5]. For traces of $UO_2(ClO_4)_2$ in presence of $HClO_4$ the law we should expect is

Partition coefficient $\propto f_0(ClO_4^-)^2 y_\pm^3 [TBP]^2/y$, where

f_0 is the fraction of UO_2 present in the aqueous phase as UO_2^{2+} (i.e. uncomplexed by ClO_4^-);

(ClO_4^-) is the true (as opposed to stoicheiometric) perchlorate ion concentration in the aqueous phase;

$y_\pm$ is the mean molar activity coefficient of fully ionized $UO_2(ClO_4)_2$ in the aqueous phase;

[TBP] is the activity of the TBP; and

y is the molar activity of $[UO_2(ClO_4)_2 \cdot 2TBP]$ in the organic phase.

At low concentrations y will be approximately equal to unity, and will not have an important effect.

As the acid concentration is increased, extraction at first increases owing to the

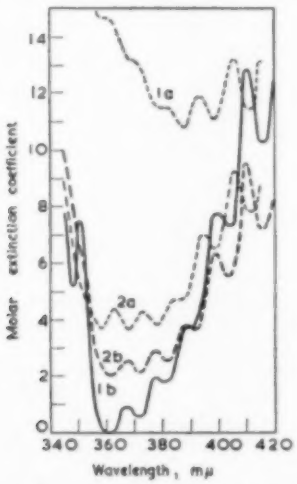

FIG. 10.—Effect of partial desiccation on absorption spectra in TBP
1a, 0·0116 M $UO_2(ClO_4)_2$, water saturated
1b, 0·00854 M $UO_2(ClO_4)_2$, partially desiccated
2a, 0·209 M $UO_2(ClO_4)_2$, water saturated
2b, 0·240 M $UO_2(ClO_4)_2$, partially desiccated.

effect of the factor $(ClO_4^-)^2$. This is enhanced by the factor $y_\pm^3$. In the nitrate system the corresponding increase is soon offset by:

(1) association between UO_2^{2+} and NO_3^- ions, which reduces f_0 below unity,

(2) incomplete ionization of nitric acid, so that (NO_3^-) falls below the stoicheiometric nitrate concentration and

(3) HNO_3 competition for the available TBP, leading to a reduction in the factor $[TBP]^2$.

In the perchlorate system, however, all these effects are of much less importance. Consequently the partition coefficient continues to rise with increasing acidity, and the rise is only ultimately checked at about 10·5 M $HClO_4$, when almost all the TBP has been complexed as $HClO_4 \cdot TBP$ (Fig. 7).

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The rate of rise of the partition coefficient with increasing acidity is very steep. For 0·5% TBP in benzene, for example, there is an increase of nearly 10^4 between 5 and 8 M $HClO_4$. The term $(ClO_4^-)^2$ would contribute a factor of only about 2·5 to this increase; the remainder must all come from the term $y_{\pm}^3$. This may seem a large effect, but it is in fact what we should expect if $y_{\pm}$ (for a trace of $UO_2(ClO_4)_2$ in $HClO_4$) lies between $y_{\pm}^2$ $HClO_4$ and $y_{\pm}$ $UO_2(ClO_4)_2$ (properties of the separate electrolytes), and rather nearer the former than the latter.

Ultimately very high partition coefficients indeed are reached, much higher than any observed for nitrate systems. Even with 0·05% TBP in benzene, a partition coefficient of nearly fifteen can be obtained at 10·5 M $HClO_4$. With ^{233}U it then becomes a little difficult to ensure that the uranium concentration is negligible in comparison with that of the TBP, and in some cases we have made a small correction to the results to allow for complexing of an appreciable fraction of the TBP as $UO_2(ClO_4)_2 \cdot 2TBP$.

The spectral data

Figs. 8, 9 and 10 demonstrate the effects on the absorption spectra of (i) varying the $UO_2(ClO_4)_2$ concentration in TBP, (ii) varying the $HClO_4$ concentration in TBP at constant $UO_2(ClO_4)_2$ concentration, and (iii) partially dehydrating the TBP phase. In the first two series, the solutions were substantially water-saturated.

If we increase the $UO_2(ClO_4)_2$ concentration, or add $HClO_4$ up to a certain point, or dehydrate the solution, we produce two main effects. Firstly, a trough appears and becomes more pronounced in the region of 370 mμ, and secondly, the vibrational peaks at 363, 373, 384, 395, . . . etc. mμ are enhanced. It would be natural to interpret these phenomena as due to suppression of the $UO_2(ClO_4)_2$ ionization, but difficulties arise when we try to correlate such an interpretation with observations in other solvents. Uranyl salts in water, for example, give spectra more like No. 4 than No. 1 in Fig. 8, although the aqueous solutions are fully ionized. Moreover, HEALY[6] has obtained results for uranyl nitrate in tri-ethyl phosphate which are completely parallel with ours, even though electrical conductivity measurements indicated but slight ionization; we have ourselves observed changes in the spectrum of uranyl nitrate in water-saturated TBP at different concentrations, comparable with those shown for uranyl perchlorate in Fig. 8 but without appreciable change in the apparent slight ionization. One possibility is that ion-triplets, $UO_2^{2+} \cdot ClO_4^- \cdot ClO_4^-$, although contributing nothing to the electrical conductivity, may yet have spectra distinct from those of true covalent molecules, $[UO_2(ClO_4)_2]$.

[6] T. V. HEALY, Private communication (1959).

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THE EXTRACTION OF NIOBIUM(V) FROM NITRIC ACID SOLUTION BY TRI-n-BUTYL PHOSPHATE (TBP)*

C. J. HARDY and D. SCARGILL
Atomic Energy Research Establishment, Harwell, Didcot, Berks

(*Received* 2 *July* 1959)

Abstract—Stable and reproducible solutions of $<10^{-7}$ M Nb in 2–12 M HNO_3 have been prepared and the extraction of niobium from these solutions by TBP has been studied. The niobium species in nitric acid solution are interpreted as a series of hydroxonitrato complexes of the hypothetical Nb^{5+} ion in slow equilibrium with solvent-inextractable, and possibly polymeric, species.

THE significance of certain complexes of niobium in solvent extraction processes for the separation of uranium and plutonium from fission products has recently been summarized.[1] Niobium-95 and zirconium-95 are the fission products which largely limit the decontamination factor attainable in tributyl phosphate (TBP)–nitric acid systems, and the behaviour of these elements in systems containing TBP and its hydrolytic and radiolytic degradation products, mono- and di-butylphosphoric acids (H_2MBP and HDBP respectively), is therefore of considerable importance.

While the extraction of zirconium by TBP from nitric acid solution has been examined in some detail,[2,3,4] the extraction of niobium has not, probably largely due to the ease with which tracer niobium becomes radio-colloidal. However, the extraction of niobium by TBP from nitric acid-fluoride systems (in which it is more tractable) has been studied by FLETCHER *et al.*[5,6] SCADDEN and BALLOU[7] studied the extraction by TBP and mixed butylphosphoric acids of zirconium and niobium from nitric acid solution containing a trace of oxalic acid. They found the mixed butylphosphoric acids effective for separating these two elements from each other and from nearly all other fission-products elements. MOORE[8] reported that niobium is irreversibly extracted from 2 M nitric acid by thenoyltrifluoroacetone. The behaviour of niobium-95 in nitric acid solution has also been examined with ion exchange resins by SCHUBERT and RICHTER,[9] and by PARAMONOVA and KOLYCHEV.[10]

We have prepared stable and reproducible solutions of $<10^{-7}$ M Nb in 2–12 M HNO_3 and now report details of the extraction of niobium from these solutions by TBP.

* Based on work reported in AERE C/R 2835 (1959).

[1] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. WAIN and J. WOODHEAD, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, 15P/31.
[2] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[3] D. F. PEPPARD, G. W. MASON and J. L. MAIER, *J. Inorg. Nucl. Chem.* **3**, 215 (1958).
[4] A. S. SOLOVKIN, *Zh. Neorg. Khim.* **2**, 611 (1957); See *Trans. Contents List No.* 104, p. 143, (1957).
[5] D. F. C. MORRIS, A. G. WAIN and J. M. FLETCHER, AERE C/R 1391 (1954).
[6] J. M. FLETCHER, D. F. C. MORRIS and A. G. WAIN, *Trans. Inst. Min. Metall.* **65**, 487 (1955).
[7] E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
[8] F. L. MOORE, *Analyt. Chem.* **28**, 997 (1956).
[9] J. SCHUBERT and J. W. RICHTER, AECD 2813 (declassified) 1950.
[10] V. I. PARAMONOVA and V. B. KOLYCHEV, *Zh. Neorg. Khim.* **1**, 1896 (1956); see *Chem. Abstr.* **51**, 6272c (1957).

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EXPERIMENTAL

The preparation of stable and reproducible solutions of ^{95}Nb in nitric acid

A mixture of ^{95}Nb/^{95}Zr was obtained from the Radiochemical Centre, Amersham, and the ^{95}Nb was separated and purified by solvent extraction with thenoyltrifluoroacetone.[11] Nitric acid solutions of ^{95}Nb for use in the initial experiments were prepared by dilution of aliquots of the solution from the above separation, and were centrifuged. Examination of these solutions by solvent extraction did not give reproducible distribution coefficients for ^{95}Nb and indicated that the species in solution were not in true equilibrium. Stock solutions were therefore prepared from these by heating to 100°C for 1 hr in a stoppered silicone-treated glass tube in a water-bath. The solutions were centrifuged before and after heating in order to remove any insoluble particles, and were stored in silicone-treated glassware or in polythene. With this method of preparation the behaviour of ^{95}Nb on solvent extraction was found to be reproducible and the solutions did not deposit appreciable amounts of ^{95}Nb activity on the walls of the containers over periods of several weeks.

Pre-treatment of the solvent

Pure dry TBP was prepared from the commercial product by heating one volume with four volumes of N/10 alkali, and distilling off two volumes of the aqueous phase in a stream of air. The TBP was separated from the remaining alkaline solution, washed with water, dried under vacuum at 40–50°C, and stored in a dark glass stoppered bottle. Solutions of TBP in kerosene were freshly conditioned with the appropriate nitric acid solution (three successive equal-volume equilibrations) for each series of experiments.

Apparatus and distribution coefficient measurements

The equilibration of the solvent and aqueous phases was initially carried out with a polythene stirrer in a polythene tube, but the results were not reproducible, especially with different volume ratios of solvent phase to aqueous phase, when the stirring efficiency was low. Attack of the polythene by the solvent was also suspected, and later experiments were carried out in silicone-treated glass apparatus.

The distribution coefficient of ^{95}Nb (D_{Nb}) between solvent and aqueous phases was measured by γ-counting of aliquots of the solvent and aqueous phases evaporated to dryness on stainless steel trays, using a γ-scintillation counter with a standard aluminium-lead absorber.

$$D_{Nb} \text{ is defined as } \frac{\gamma \text{ counts/min in organic phase}}{\gamma \text{ counts/min in equal volume of aqueous phase}}$$

Equal volumes of solvent and aqueous solutions (1–2 ml) were used in all distribution experiments unless stated otherwise, and the phases were separated by centrifugation before removing aliquots for counting. The experiments were carried out at room-temperature (approximately 20°C), and the stirring time necessary to reach equilibrium was determined for each system.

RESULTS

The variation of D_{Nb} with stirring time

D_{Nb} reached a constant value after approximately 3 min stirring of TBP/kerosene solutions with various concentrations of nitric acid. A stirring time of 5 min was therefore used in all the experiments.

The determination of the relative proportions of extractable and inextractable niobium species

The proportion of TBP–inextractable niobium in a given HNO_3 solution was determined by extractions with 50% TBP by MARTIN technique,[12] i.e. with varying ratios of solvent phase volume to aqueous phase volume. The concentration of the niobium in the organic phase was plotted as ordinate against the concentration of niobium

[11] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **9**, 322 (1959).
[12] F. S. MARTIN, AERE C/R 816 (1951).

in the aqueous phase as abscissa. For a solution containing a number of extractable species in rapid equilibrium a straight line is obtained which passes through the origin. For a solution containing extractable species in equilibrium together with one

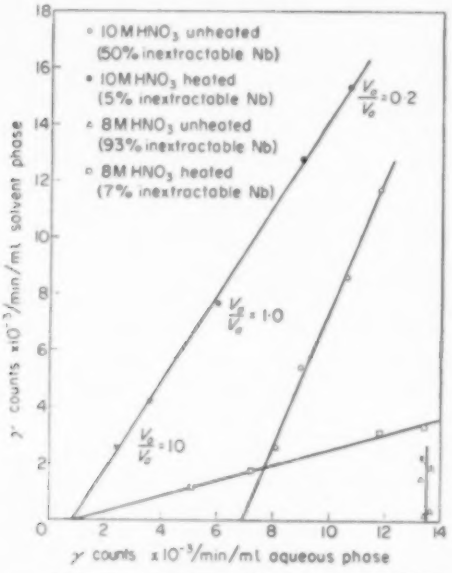

FIG. 1.—The effect of heating on the amount of TBP-inextractable niobium in nitric acid solution.

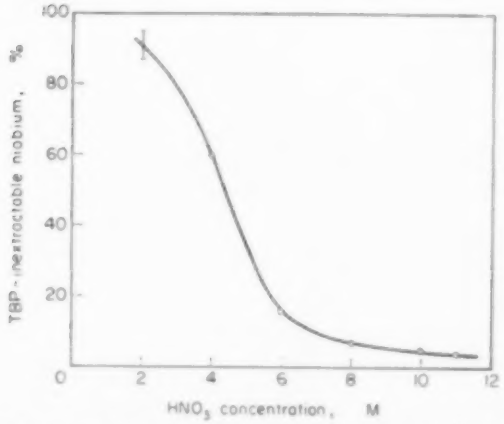

FIG. 2.—Variation in the amount of TBP-inextractable niobium with the nitric acid concentration.

(or more) inextractable species not in rapid equilibrium a straight line cutting the abscissa is obtained, the intercept giving the proportion of the inextractable species.

Results for solutions in 8 and 10 M HNO_3 before and after heating them for 1 hr at 100°C, are shown in Fig. 1. The variation in the amount of this inextractable niobium with the [HNO_3] in heated stock solutions is shown in Fig. 2.

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The variation of D_{Nb} with the concentration of TBP *and* HNO_3

The variation of D_{Nb} with $[HNO_3]$ for extraction by 50% TBP is shown in Fig. 3. The difference between the forward D_{Nb} and the strip D_{Nb} at low $[HNO_3]$ is largely due to the presence of the inextractable niobium during the forward extraction. However, the small amount of ^{95}Zr impurity in the ^{95}Nb contributes to the increased strip distribution coefficient because zirconium has a much higher partition coefficient[2] than the extractable niobium. The true strip partition coefficients (K_{Nb}) for

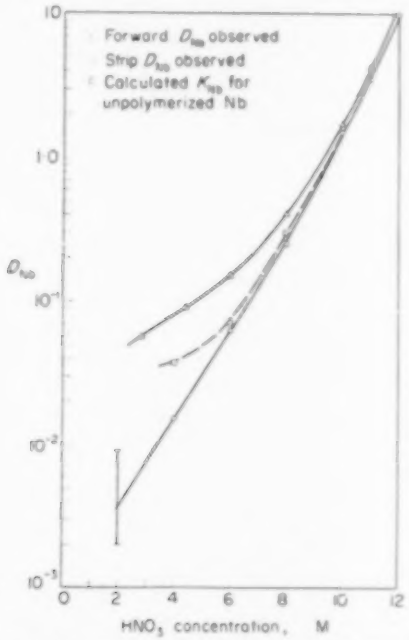

FIG. 3.—Distribution of niobium between 50% TBP and nitric acid.

50% TBP have been calculated (Fig. 3) from the forward D_{Nb}, the per cent inextractable niobium, X (from Fig. 2), the per cent zirconium impurity, and the K_{Zr} (calculated for 50% TBP from the data at 19 per cent[2] assuming a square law dependence on [TBP]) by the following equation:

$$D_{Nb} = \frac{\dfrac{(100 - X) \cdot K_{Nb}}{1 + K_{Nb}} + \dfrac{\%\,Zr \cdot K_{Zr}}{1 + K_{Zr}}}{X + \dfrac{\%\,Zr}{1 + K_{Zr}} + \dfrac{(100 - X)}{1 + K_{Nb}}}$$

The variation of D_{Nb} with $[HNO_3]$ at other TBP concentrations is shown in Fig. 4, and the variation of D_{Nb} with [TBP] at constant $[HNO_3]$ in Fig. 5. The slopes of the latter plots are of the order of 2·6 at >20% TBP but below 20 per cent they tend towards a lower slope, It is therefore likely that <2·6 molecules of TBP per Nb are present in the complex extracted into the organic phase at low TBP concentration.

D_{Nb} increases with the 2nd–3rd power of the stoichiometric $[HNO_3]$ but no firm

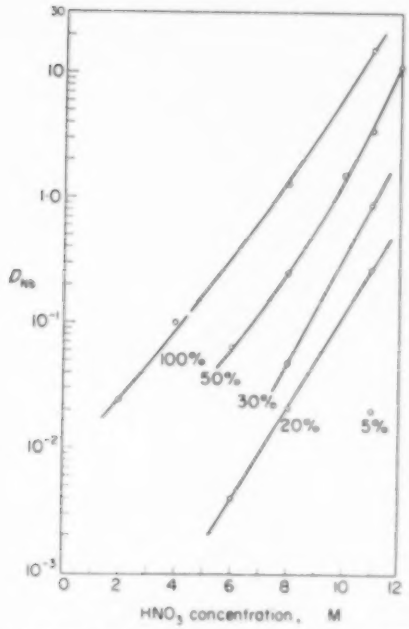

FIG. 4.—Variation of D_{Nb} with the concentrations of TBP and HNO_3.

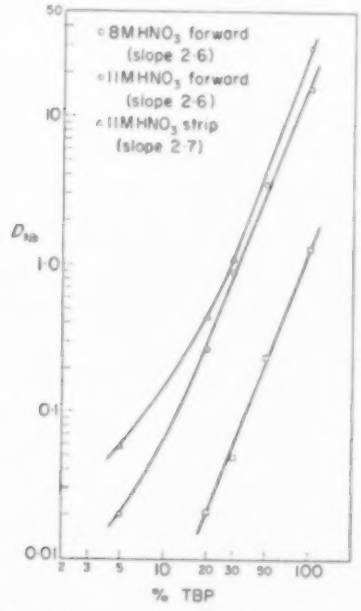

FIG. 5.—Variation of D_{Nb} with TBP concentration.

conclusions can be drawn from Figs. 3 and 4 as to the dependence of D_{Nb} on $[NO_3^-]$ because the experiments were not carried out at constant ionic strength and constant $[H^+]$. The determination of the dependence of D_{Nb} on $[NO_3^-]$ and $[H^+]$ separately would have been useful in elucidating the nature of the extractable species, but this is difficult to carry out due to the low values of D_{Nb} in the range 1–6 M HNO_3 and the ease of hydrolysis of niobium at low $[H^+]$.

DISCUSSION

The presence of both extractable (probably "simple" ionic) species and inextractable (probably complex polymeric) species of niobium is indicated from the solvent extraction results. The relative amounts of these species depend upon the concentrations of niobium and of HNO_3 and also upon the history of the solution. The behaviour of niobium in HNO_3 solution can best be interpreted at present on the basis of the existence of hydroxo-nitrato complexes of the hypothetical Nb^{5+} ion (compare protactinium in HNO_3 solution[13]).

Equilibria slow	Equilibria fast i.e. labile complexes		
	cationic species	neutral species	anionic species
Polymers ⇌	$Nb(OH)_4^+$ ⇌ $Nb(OH)_3^{3+}$ $Nb(OH)_2^{3+}$ (= NbO^{3+}) etc.	$Nb(OH)_4NO_3$ ⇌ $Nb(OH)_2(NO_3)_2$ $Nb(OH)_3(NO_3)_2$ etc.	$Nb(OH)_3(NO_3)_3^-$
Slight physical adsorption by cation and anion resins	adsorbed by cation resin	—	adsorbed by anion resin
Not extracted by TBP or by dibutylphosphoric acid (HDBP)[14]	extracted by HDBP at low $[HNO_3]$	extracted by TBP; extracted by HDBP at high $[HNO_3]$	probably extracted by TBP as acid form at high $[HNO_3]$

Stable and reproducible solutions of these niobium species in HNO_3 can be prepared provided that (i) they are heated for at least 1 hr at 100°C, (ii) the [Nb] is $<10^{-7}$ M, and (iii) that the $[HNO_3]$ is >2 M. At higher [Nb], polymers form more readily and are more stable, e.g. at 10^{-5} M large irreproducible amounts of polymer are present even after heat-treatment in strong HNO_3. At <2 M HNO_3 (even after heat-treatment of $<10^{-7}$ M Nb solutions) the amount of polymer is >95 per cent.

A few ion-exchange experiments which have been carried out on these niobium solutions[14] indicate a slow approach to equilibrium and the adsorption of Nb by both cation and anion resins (there is a greater adsorption at 6 M HNO_3 by the cation resin than by the anion resin). PARAMONOVA and KOLYCHEV[10] concluded from their experiments with ion-exchange columns and dialysis membranes that ^{95}Nb (at $\sim 10^{-14}$ M) existed in 0·01–2 M HNO_3 solution in two different forms, that the adsorption was largely physical and was approximately the same for both cation and anion resins, and that the amount of dialysable niobium increased with acid

[13] C. J. HARDY, J. M. FLETCHER and D. SCARGILL, *J. Inorg. Nucl. Chem.* 7, 257 (1958).

concentration. These results at a "true" tracer concentrations of ^{95}Nb agree reasonably well with the present solvent extraction and earlier ion-exchange results[14] in which inactive Nb was added to give a final [Nb] $\sim 10^{-7}$ M.

TBP does not extract the polymeric niobium species, and gives lower distribution coefficients for unpolymerized niobium than for U(VI), Pa(V) and Zr(IV) under similar conditions[1,13] e.g.

Element	U(VI)	Pa(V)	Zr(IV)	Nb(V)
D between 20% TBP and 2 M HNO_3	10	0·2	0·05	$<5 \times 10^{-4}$
6 M HNO_3	30	1·0	0·9	4×10^{-3}
12 M HNO_3	10	5	35	0·6

It is known that in TBP processes for the treatment of irradiated fuels, fission product niobium (usually at $<10^{-5}$ M) slightly contaminates the separated uranium and plutonium. The facts presented in this paper show that this contamination cannot be due to the direct extraction of a TBP-Nb complex. There are however other probable explanations, for instance, the entrainment of colloidal niobium, or the extraction of complexes of niobium with (i) mono- and di-butylphosphoric acids arising from the degradation of the TBP and (ii) impurities in, or degradation products from, the kerosene diluent, e.g. unsaturated hydrocarbons, aldehydes or ketones.

Acknowledgement—The authors would like to thank Dr. J. M. FLETCHER for helpful advice during the course of the work and in the preparation of the manuscript.

[13] C. J. HARDY and D. SCARGILL, AERE C/R 2835 (1959).

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J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 181 to 191. Pergamon Press Ltd. Printed in Northern Ireland

RADIOACTIVE DECAY PROPERTIES OF ^{238}Am, ^{239}Am, ^{240}Am, ^{240}Cm AND ^{241}Cm*

R. A. GLASS,† R. J. CARR‡ and W. M. GIBSON§
Lawrence Radiation Laboratory, University of California, Berkeley, California

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Abstract—Some electron-capture and α-decay properties of neutron-deficient americium and curium isotopes have been investigated using 2π proportional counting, scintillation spectrometry, and α-pulse analysis. The results for ^{238}Am include a new half-life of 1·86 hr and identification of γ-rays of ~370 keV (~12%), 580 keV (~29%), ~950 keV (~2%), 980 keV (~76%), and ~1350 keV (~17%). The data on ^{239}Am (half-life 12·1 hr) indicate γ-rays of 225 keV (~30%) and 275 keV (~20%) with a new α-particle energy of 5·77 MeV and abundance of $5{\cdot}0 \times 10^{-2}$ per cent. For ^{240}Am (half-life 51·0 hr) γ-rays of 900 keV (~23%) and 1000 keV (~77)% and a negatron branching limit of $\leq 6 \times 10^{-6}$ per cent were established. For ^{240}Cm a new α-particle energy of 6·26 MeV was established. For ^{241}Cm a new alpha particle energy of 5·95 MeV and abundance of 0·96 per cent and a γ-ray of 478 keV (97%) were established. Counting efficiencies for the 2π-geometry methane-flow proportional counter are 60, 90 and 82 per cent for the electron-capture decay of ^{239}Am, ^{240}Am and ^{241}Cm, respectively. These are in the range of values found for other β-unstable isotopes of heavy elements.

The data on ^{238}Am and ^{240}Am are consistent with a rule that only levels ~1000 keV and higher in even-even plutonium isotopes are populated by relatively fast β-transitions (log *ft* 5–8) in the decay of odd-odd americium and neptunium isotopes.

THE present investigation of decay properties of neutron-deficient americium and curium isotopes was undertaken during the course of a series of cross-section measurements[1] in order to obtain preliminary data on the decay schemes and counting efficiencies (on a 2π-geometry windowless proportional counter).

The γ-ray and α-particle data obtained are of interest from the standpoint of correlation with the systematics of forbiddenness for β-decay and hindrance factors for α-decay.[2–6] In most cases, however, more detailed studies with α- and β-spectrographs and further coincidence studies are needed to complete the decay schemes.

The calculation of absolute cross-sections or α-particle and γ-ray intensities requires that absolute disintegration rates of the nuclides in question be determined. This has been a particularly troublesome problem for nuclides which decay by

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† Present address: Stanford Research Institute, Menlo Park, California.
‡ Present address: Department of Chemistry, State College of Washington, Pullman, Washington.
§ Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] For a study of helium-ion reactions in ^{238}Pu, ^{239}Pu, and ^{242}Pu, see R. A. GLASS, R. J. CARR, J. W. COBBLE and G. T. SEABORG, *Phys. Rev.* **104**, 434 (1956). For a study of helium-ion reactions in ^{237}Np and deuteron reactions in ^{239}Pu see W. M. GIBSON. Thesis, University of California (1957), also reproduced in Unpublished Report UCRL-3493, (1956).

[2] For various correlations of heavy element decay properties see G. T. SEABORG, *The Transuranium Elements*, Yale University Press, New Haven (1958).

[3] R. W. HOFF and S. G. THOMPSON, *Phys. Rev.* **96**, 1350 (1954).

[4] I. PERLMAN and J. O. RASMUSSEN, *Handbuch der Physik* Vol. 42, p. 109. Springer-Verlag (1957) also reproduced as Unclassified Report UCRL-3424, (1956).

[5] F. S. STEPHENS, F. ASARO and I. PERLMAN, *Phys. Rev.* **113**, 212 (1959).

[6] B. R. MOTTELSON and S. G. NILSSON, *Mat. Fys. Skr. Dan. Vid. Selsk.* **1**, No. 8 (1959).

orbital-electron capture. Calibration of a given type of counting system (preferably one of high geometry and low sensitivity to sample preparation method), however, allows one to estimate disintegration rates of other samples of the same nuclide with some confidence. In addition, repeated calibrations for as many different nuclides as possible form a basis for estimating disintegration rates of other nuclides. In the course of these studies counting efficiencies were determined for weightless samples of a number of nuclides on a 2π windowless methane-flow proportional counter.*

EXPERIMENTAL PROCEDURES

Targets of 1–100 mg of plutonium-239 oxide were bombarded with 27 and 35 MeV protons in the 184 in. synchrocyclotron to produce ^{238}Am; with 15–20 MeV deuterons in the 60 in. cyclotron to produce ^{239}Am and ^{240}Am; and with 30–40 MeV helium ions in the 60 in. cyclotron to produce ^{240}Am, ^{240}Cm and ^{241}Cm. Plutonium-239 targets of high isotopic purity were employed to avoid ^{241}Am α-activity contamination from the decay of ^{241}Pu present in ordinary plutonium. Chemical separations were performed to separate the curium and/or americium fractions from the target material, fission products, and unwanted spallation products. For the counting efficiency determinations the plutonium daughter activities were separated from the americium fraction after suitable growth periods.

Electron-capture isotopes were counted in a windowless 2π-geometry gas-flow proportional counter. Natural gas (mainly methane) was used as the counting gas. The sample, mounted on a 2·5 cm diameter platinum disk, was placed inside the counting chamber† at a distance of about 4 cm from a 1 mil centre wire. The counter was operated on the proportional plateau at about 4,000 V. Effect of sample preparation upon the counting efficiency was studied by comparing the counting rates of equivalent samples mounted by (1) evaporation of a carrier-free aqueous solution, (2) volatilization from a tantalum filament in vacuo at ~1800°C or (3) electrodeposition from neutral ammonium chloride solution.[7] Under proper conditions, the last two methods result in essentially weightless samples of <10 μg/cm^2 mass, whereas the first method may lead to 30–50 μg/cm^2 or greater. It was found that the sample thickness (up to ~30 μg/cm^2) becomes critical only when a sizeable fraction of the counting rate for a nuclide depends on low-energy Auger electrons. For example successive volatilization of about 10 μg amounts of tantalum onto a weightless sample of ^{243}Am (which is known[8] to have a high abundance of several hundred kilovolt conversion electrons) reduced the counting rate by 10 per cent only after 50 μg/cm^2 had been transferred. Counting rates of ^{236}Np are also reasonably independent of sample thickness.[9] On the other hand, ^{237}Pu, which decays mostly (60 per cent) to the ground state, counts most efficiently when electroplated, slightly less efficiently when vaporized, and considerably less efficiently when evaporated.[10]

A Frisch grid ionization chamber and a 50 channel pulse-height analyser were used for alpha spectroscopy. γ-spectra were determined with a scintillation counter employing a 1½ (dia.) × 1 in. thallium-activated sodium iodide crystal and a 50 channel pulse-height analyser. Photopeak counting efficiencies and geometry factors tabulated by KALKSTEIN and HOLLANDER were used.[11] In the γ–γ coincidence measurements the energy of the gating pulse from a second sodium iodide detector was determined by analysis in a single channel pulse-height analyser. The resolving time of the coincidence apparatus was 2 μsec.

In all of the measurements, probable errors have been assigned on the basis of estimated systematic accuracy as well as the precision of the data.

* Previous techniques used include measuring K X-ray counting rates (which necessitates detailed knowledge of the decay-scheme), measuring counting rates in a 4π-geometry proportional counter, and measuring disintegration rates of α-particle emitting daughters produced from decay of the electron-capture parents. The last of these methods is the most accurate and was employed in this investigation.

† The detector used was manufactured by the Radiation Counter Laboratories of Chicago Illinois and carried the trade name "Nucleometer".

[7] A. CHETHAM-STRODE, JR., Thesis University of California (1956) also available as Unpublished Report UCRL-3322 (1956).

[8] W. G. SMITH, W. M. GIBSON and J. M. HOLLANDER, *Phys. Rev.* **105**, 1514 (1957).

[9] W. M. GIBSON, Thesis University of California (1957) also available as unpublished Report UCRL-3493 (1956).

[10] R. VANDENBOSCH, Unpublished data (1955).

[11] M. I. KALKSTEIN and J. M. HOLLANDER, Unpublished Report UCRL-2647 (1954) (unpublished).

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RESULTS

Americium-238

The electron-capture decay of ^{238}Am is of unusual interest among the heavy nuclides because the energy available for this process is almost uniquely high (2·26 MeV, estimated[12] from systematics) for known nuclides away from closed nucleon shells. The lower-level structure of the daughter nuclide has been studied through the alternative routes of α-decay[7] of ^{242}Cm and negatron decay[13] of ^{238}Np with results which are of interest in terms of the collective model of the nucleus.[14]

Prominent γ-rays of 580 ± 25 keV and 980 ± 40 keV were observed in the americium fraction from bombardments with both 27 MeV and 35 MeV protons

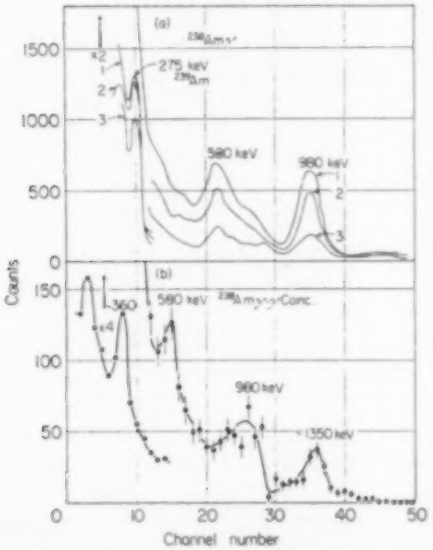

FIG. 1.—γ-Ray spectra of ^{238}Am. (a) The direct spectrum measured at three different times, (b) spectrum of γ-rays in coincidence with γ-rays of 580 keV. The apparent self-coincidence peak at 580 keV is probably due to coincidences between 580 keV γ-rays and Compton-scattered electrons from initially 980 keV γ-rays.

(see Fig. 1a). A half-life of 1·86 ± 0·09 hr was obtained by following the decay of the 580 keV and 980 keV photon peaks. (The previous value[15] (2·1 hr) was determined from resolution of a three component decay curve.) The assignment of these two high-energy γ-rays to ^{238}Am rather than ^{237}Am was made because their intensity relative to the 6·01 MeV α-particles[15] of ^{237}Am decreased appreciably when the proton bombarding energy was increased from 27 to 35 MeV. The γ-ray spectrum in the region of 150–400 keV was completely obscured by the very prominent photopeaks of 225 keV and 275 keV belonging to ^{239}Am. However, photopeaks having 1·9 hr components were observed with energies of 14 keV, 18 keV and 102 keV. The

[12] R. A. GLASS, S. G. THOMPSON and G. T. SEABORG, *J. Inorg. Nucl. Chem.* **1**, 3 (1955).
[13] J. O. RASMUSSEN, H. SLÄTIS and T. O. PASSELL, *Phys. Rev.* **99**, 42 (1955); J. O. RASMUSSEN, F. S. STEPHENS, O. STROMINGER and B. ÅSTRÖM, *Ibid.* **99**, 47 (1955).
[14] A. BOHR and B. R. MOTTELSON, *Kgl. Danske Viden Skal. Selskab. Mat. -fys. Medd.* **27**, 16 (1953).
[15] Ph.D. thesis of G. H. HIGGINS, Thesis, University of California (1952); also available as Unpublished Report UCRL-1729 (1952).

first two of these, resolved with a xenon-filled proportional counter, correspond to the L_α and L_β X-rays of plutonium; the last is essentially all plutonium K X-rays, but also may contain a small contribution from the highly converted 104 keV γ-ray corresponding to a transition between levels of ^{238}Pu known from ^{238}Np and ^{242}Cm decay studies.

In order to establish the relationships between the high-energy γ-rays in the decay scheme, γ-γ coincidence studies were made. In the course of these measurements new γ-rays of 1350 keV and 370 keV were found. The decay of all coincidence peaks

TABLE 1.—AMERICIUM-238 γ-γ COINCIDENCES*

Gate (keV)	Coincident γ-rays (signal) (keV)
980	~370, 580, ~950
580	~360, 580, 980, ~1350
~1350	~580

* The energy measurements of the coincident γ-rays are approximate since the inherent accuracy of the instrument used is only about 4 per cent and the counting rates were very low (of the order of 3 counts per minute for some of the peaks). Further, the short half-life of the nuclide drastically limits the amount of time available for the measurements.

was checked to confirm their assignment to ^{238}Am. The observations are summarized in Table 1, and the gamma spectrum coincident with the 580 keV γ-ray is shown in Fig. 1b.

The apparent self coincidence of the 580 keV γ-ray is probably not real. Radiations in the 580 keV region in coincidence with the 580 keV photopeak are believed to be due to the Compton edge of the 980 keV photopeak. Thus the apparent self-coincidence is probably a result of the 980–580 keV cascade. The apparent 580–360 keV coincidences may also include some contribution from electrons and photons resulting from Compton scattering of the 980 keV γ-ray.

From the gross spectra the relative intensities of the L X-rays, K X-rays, 580 keV γ-rays and 980 keV γ-rays can be calculated. The L X-ray counting efficiencies and geometry factors of HOFF[16], for the xenon-filled proportional counter were used. Corrections were made for escape peaks in the cases of the K X-rays, and Compton scattered electrons from the 980 keV γ-ray in the case of the 580 keV γ-ray. The relative intensities are: L X-rays : K X-rays : 580 keV : 980 keV = 63 : 100 : 29 : 78.

It is reasonable to assume that about one K X-ray is emitted per disintegration in order to establish rough absolute intensities. This is based on: (1) the expectation that the 102 keV γ-radiation that has been observed in ^{238}Np and ^{242}Cm decay, and which has the same energy as K X-rays is negligible; (2) the assumption that K-shell conversion of the more energetic γ-rays is small; (3) the assumption that L-electron capture is probably small (near the theoretical limit[17] of 14 per cent) since the observed L X-rays can be accounted for by the L-shell vacancies arising from electron transitions to fill K-shell vacancies and L-shell conversion of γ-rays; and (4) the fact

[16] R. W. HOFF, Unpublished data (1954).
[17] H. BRYSK and M. E. ROSE, Unpublished Report ORNL-1830, (1955).

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that the fluorescent yield[18] of K-shell vacancies is almost 100 per cent. It will be noted later that measured K X-ray intensities (~85 per cent for ^{239}Am, ~75 per cent for ^{240}Am, and ~90 per cent for ^{241}Cm) are somewhat less than 100 per cent, although most probable errors would tend to increase these experimental values. From the assumption of one K X-ray per disintegration the intensity of the 580 keV gamma ray is determined as ~29 per cent. The 580 keV γ-ray intensity along with

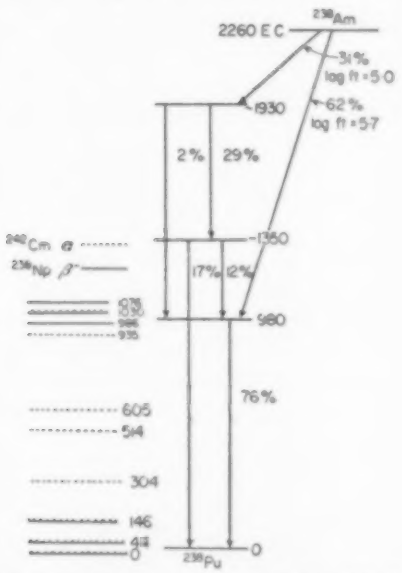

FIG. 2.—Preliminary decay scheme for ^{238}Am showing γ-ray intensities (and therefore electron-capture-branching intensities since conversion of these high energy γ-rays should be very low) based on the assumption that one K X-ray is emitted per disintegration. The unaccounted for 7 per cent decay may be due to an error in the above assumption but could also be due to branching to the ground state or to a low energy state of ^{238}Pu. The ^{238}Pu levels on the left are those populated from negatron decay to ^{238}Np and α-decay of ^{242}Cm, as listed by PERLMAN and RASMUSSEN.[6] The exact alignment of ^{238}Am associated levels is not certain due to uncertainties in energies and in the precise levels near the ground state populated by the high energy γ-rays.

the relative intensities obtained from the coincidence data allows the absolute intensities of the other γ-rays to be computed.*

The decay scheme indicated by these data is given in Fig. 2. An alternative

* Only the intensity of the 580-keV γ-ray is determined uniquely from the gross γ-ray spectra and the assumption of one K X-ray per disintegration. The intensities of the other transitions, however, can be derived on the basis of the proposed decay scheme from the gross spectral intensities and the relative coincidence intensities. The relative intensities of the 370 keV and the 580 keV γ-rays in coincidence with the 980 keV photopeak are the same as the relative intensities obtained using the 580 keV γ-rays as gating pulses. This indicates that there is little direct population by electron capture to the 1350 keV level. The intensity o the 580 keV radiations (determined to be 29 per cent from the gross spectra) must then equal the sum of the intensities of the 370 keV and the 1350 keV γ-rays. Since the relative intensities of the 370 and the 1350 keV γ-rays are established from the coincidence measurements, the absolute intensities of these transitions can be calculated. To assign intensities to the ~950 keV and 980 keV transitions, one may use the relative intensities of the 580 keV and ~950 keV gamma rays in coincidence with the 980 keV photopeak (taking into account that either the 980 keV or ~950 keV γ-ray may be acting as a gating pulse and either appearing in the coincidence spectrum). Since the 580–980 keV cascade has been fixed at 12 per cent, the ~950 keV γ-ray intensity is calculable. Finally, the 980 keV γ-ray intensity is equal to the difference between the gross 980 keV γ-ray intensity and the ~950 keV γ-ray intensity.

[18] P. R. GRAY, *Phys. Rev.* **101**, 1306 (1956).

possibility would have the 580 keV and the ~370 keV γ-rays depopulate the 980 keV level; that is, in a path parallel to the lower rather than the upper ~950 keV γ-transition (a 605 keV level has been observed in ^{238}Pu from the α-decay of ^{242}Cm.[7]) However, the observed 580 keV–~1350 keV coincidences as well as the fact that the 605 keV level (or any near by level) is not observed in the negatron decay of ^{238}Np, either from direct population or from cascade from the levels near 1 MeV, have led us to place the 580 keV γ-transition solely in the high-energy branch. Also shown for comparison purposes, is the level diagram of ^{238}Pu as indicated by the decay of ^{238}Np and ^{242}Cm. It should be noted that in these studies many transitions were observed between the band of levels at ground and that near 1 MeV. There are at least four and possibly five γ-transitions between 927 keV and 1029 keV from ^{238}Np. These would appear as a single photopeak in the equipment used in this study. It is highly probable, therefore, that the 980 keV γ-ray of ^{238}Am is also complex. Indeed, it may be that all the observed γ-rays are complex and that the levels indicated are really bands of levels.

Approximate log *ft* values* of 5·0 and 5·7 were estimated to the ~1930 keV level and the 980 keV level, respectively, corresponding to allowed transitions. It is perhaps worth pointing out a few observations about the energy level of ~1930 keV (which is one of the highest ever observed in decay studies in the heavy element region). If the band of levels around 1 MeV corresponds to a first vibrational excitation, according to the collective model a second vibrational band is expected[14] at about twice this energy.

Americium-239

The level scheme of ^{239}Pu has been characterized in extensive studies of the β-decay[20] of ^{239}Np and the alpha decay[21] of ^{243}Cm. In addition, the conversion-electron spectrum associated with the electron-capture decay of ^{239}Am has been determined,[8] with results of value for correlation with the present γ-ray studies. γ-rays in coincidence with the alpha particles of ^{239}Am have also been reported.[22]

Intense samples containing ^{239}Am and ^{240}Am were counted repeatedly over many half-lives of both isotopes in the proportional counter giving a value of 12·1 $\pm$ 0·4 hr for the half-life of ^{239}Am.

The presence of ^{240}Am in the samples limited the accuracy of counting efficiency determinations for ^{239}Am. Since the daughters of both ^{239}Am and ^{240}Am (^{239}Pu and ^{240}Pu respectively) have almost the same α-particle energy, a growth vs. time analysis of the α-radiations of this energy was necessary. The proportional counting efficiency for ^{239}Am (volatilized onto platinum from a tungsten filament) obtained from a single experiment was 60 $\pm$ 20 per cent.

γ-Rays of 225 $\pm$ 10 keV and 275 $\pm$ 33 keV with the 12 hr half-life were observed in the gross γ-spectra. Abundances obtained (based on a 60 per cent proportional counter efficiency) were: *K* X-rays, 85 $\pm$ 30 per cent; 225 keV γ-rays, 30 $\pm$ 15 per

* The log *ft* calculations for ^{238}Am and other isotopes were made using the graphs of BRYSK and ROSE[17] for *K*, L_I, and L_{II} electron capture. These lead to log *ft* values about 0·1 to 0·2 lower than those calculated from the nomogram for *K* electron capture. (see ref. 19).

[19] S. A. MOSZKOWSKI, *Phys. Rev.* **82**, 35 (1951).

[20] J. M. HOLLANDER, W. G. SMITH and J. W. MIHELICH, *Phys. Rev.* **102**, 740 (1956); D. ENGELKEMEIR and L. B. MAGNUSSON, *Ibid.* **99**, 135 (1955).

[21] I. PERLMAN and F. ASARO, *Ann. Rev. Nucl. Sci.* **4**, 157 (1954).

[22] F. ASARO, F. S. STEPHENS, JR., W. M. GIBSON, R. A. GLASS and I. PERLMAN, *Phys. Rev.* **100**, 1541 (1955).

cent; 275 keV γ-rays, 20 $\pm$ 10 per cent. These abundances are somewhat at variance with the conversion electron data;[8] principally in that the K X-ray intensity is low. Considering K-X ray counting difficulties in this experiment and the proportional counting efficiency uncertainties, however, it is believed that the difference is not significant.

Results of γ-γ coincidence studies are given in Table 2.

TABLE 2.—AMERICIUM-239 γ–γ COINCIDENCES

Gate	Coincident γ-rays (signal) (keV)
K X-rays (keV)	K X-rays, ~225, ~275
~225	K X-rays, ~225, ~275
~275	K X-rays, (~180?), ~225

These measurements confirm the cascade relationship that a 225 keV γ-ray leads to a level depopulated by 225 keV and 275 keV γ-rays.

These data have not been analysed further because of the uncertainty in the intensity measurements and because log ft values and level assignments have been treated elsewhere.[8]

Well resolved α-particles from ^{239}Am were observed in samples from two bombardments. The α-energy was redetermined as 5·77 $\pm$ 0·02 MeV.

The per cent of ^{239}Am decays proceeding by α-particle emission was evaluated in duplicate experiments with results of 5·0 $\times$ 10^{-3} and 4·9 $\times$ 10^{-3} (based on a proportional counting efficiency of 60 per cent for electron capture decay). The best value is taken as (5·0 $\pm$ 1·0) $\times$ 10^{-3}, corresponding to a partial α-half-life of 28 $\pm$ 5 years. The hindrance factor is 2·6 for this α-group, to be compared with values[4] of 1·2 and 1·1 for the α-particle groups in highest abundance of ^{241}Am and ^{243}Am, respectively.

Americium-240

The electron capture decay characteristics of ^{240}Am are of interest for comparison with the decay of ^{238}Am, since both isotopes are odd-odd nuclei and decay to even-even plutonium isotopes. For the levels of ^{240}Pu, information has been obtained through study of the α-decay of ^{244}Cm[23] and negatron decay of the 7·3 min[24] and 60 min[25] isomers of ^{240}Np.

The half life of ^{240}Am was determined to be 51·0 $\pm$ 0·5 hr by proportional counting.

The electron-capture proportional counting efficiency was determined for an evaporated sample for one plutonium daughter "growth" period (following one bombardment) and for vaporized samples for two "growth" periods (following a second bombardment). The values derived were 91, 109 and 67 per cent, respectively, leading to an average value of 90 $\pm$ 15 per cent.

Photopeaks of 900 $\pm$ 20 keV, 1000 $\pm$ 30 keV, and 1400 $\pm$ 50 keV, decaying with a 51 hr half-life were observed in the gross α-spectra. The abundances obtained from

[23] J. P. HUMMEL, Thesis University of California (1956); also available as Unpublished Report UCRL-3456 (1956).
[24] J. D. KNIGHT, M. E. BUNKER, B. WARREN and J. W. STARNER, *Phys. Rev.* **91**, 889 (1953).
[25] R. M. LESSLER, Thesis University of California (1959); also available as Unpublished Report UCRL-8439 (1958).

a series of independent measurements (all based on a 90 per cent proportional counting efficiency) were: L X-rays, 55 ± 10 per cent; K X-rays, 75 ± 15 per cent, 900 keV, 23 ± 15 per cent; 1000 keV, 77 ± 20 per cent; and 1400 keV < 10 per cent. The electron-capture counting efficiency uncertainty is not included in the estimated probable errors.

The partial decay scheme suggested by the γ-ray measurements is shown in Fig. 3, together with ^{240}Pu levels populated by α-particle and negatron decay. Values of

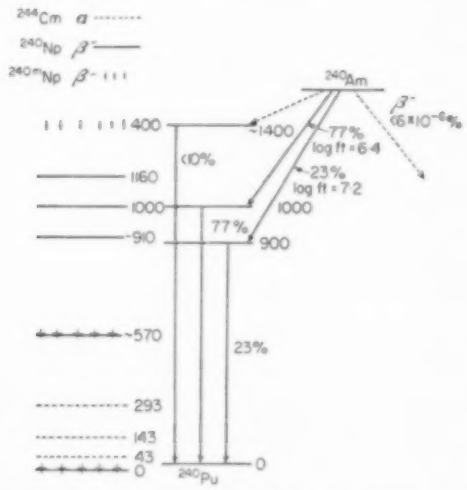

FIG. 3.—Preliminary decay scheme for ^{240}Am showing γ-ray intensities (and therefore electron capture branching intensities since conversion of the high energy γ-rays is expected to be negligible) based on a 2π-proportional counting efficiency of 90 per cent. The 1000 keV and 900 keV γ-rays could possibly proceed from the same level and populate the 43 and 143 keV levels, respectively. The ^{240}Pu levels on the left are those populated from negatron decay of ^{240}Np[25] and ^{240m}Np,[20] and α-decay of ^{244}Cm.[22] The alignment of ^{240}Am associated levels is uncertain due to uncertainties in energy measurement and in the precise levels near the ground state populated by the high energy γ-rays.

log ft for decay to the 900 keV and 1000 keV levels based on this tentative decay scheme are 7·2 and 6·4, respectively, corresponding to allowed hindered or first forbidden unhindered transitions. Both electron-capture decay branches agree with correlations for first forbidden electron capture transitions of HOFF and THOMPSON[3].

It is interesting to note that levels around 1000 keV (possibly corresponding to a vibrational band) are populated in both electron capture and negatron decay to both ^{238}Pu and ^{240}Pu. A level at about 1400 keV is also common to ^{238}Am and ^{240}Am decay.

A search was also made for negatron branching in ^{240}Am, since the results of closed cycle calculations[12] of heavy-element decay energies are ambiguous concerning the relative β-instability of ^{240}Am and ^{240}Cm. The calculations indicate that electron capture of ^{240}Cm is exoergic by 60 ± 100 keV (neglecting the electron binding energy). Experimentally, HIGGINS[15] has searched for both negatron emission of ^{240}Am and orbital electron capture of ^{240}Cm and on the basis of his negative results, has set upper limits of 2×10^{-3} per cent negatron emission for ^{240}Am and 0·5 per cent electron capture for ^{240}Cm. In the present work, a sample of ^{240}Am decaying at the rate of $4{\cdot}6 \times 10^6$ disintegrations per min was prepared. After the ^{240}Am had decayed,

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an upper limit of 0·02 disintegrations per min was set for α-particle emission at 6·26 MeV, the energy of ^{240}Cm α-particles. This limit corresponds to an upper limit of 6×10^{-6} per cent for the negatron-decay branching of ^{240}Am and a lower limit of 1×10^{5} years for the partial half-life for this process.

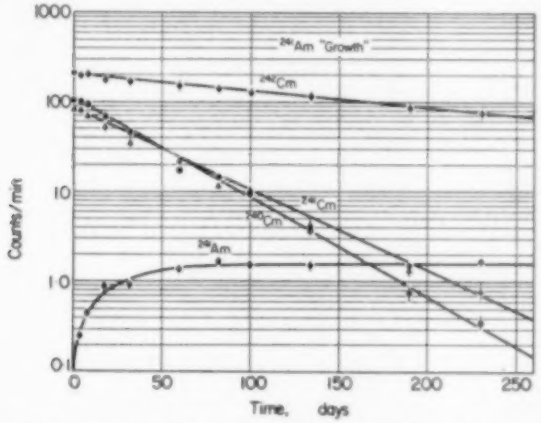

FIG. 4.—Growth of ^{241}Am α-activity into a chemically purified curium fraction. The curium was volatilized onto a platinum disk for α-pulse-height analysis. The α-activities of ^{240}Cm, ^{242}Cm and ^{241}Am represent 100 per cent of the decay of these isotopes, whereas the ^{241}Cm activity represents only 0·96 per cent of its decay.

Curium-240

This isotope is observed to decay solely by α-particle emission. The present work consisted of an attempt to improve the α-particle energy with numerous α-pulse-height analyses. The result was an energy of 6·26 ± 0·02 MeV, as compared with an earlier preliminary value of 6·2$_5$ ± 0·1 MeV.[26]

Curium-241

This isotope decays predominantly by electron capture to excited levels of ^{241}Am,* which are also populated by α-decay[7,28] of ^{245}Bk.

The electron-capture proportional-counting efficiency was determined by observing the growth of ^{241}Am α-activity in a vaporized sample of ^{241}Cm (see Fig. 4). The isotope ^{241}Cm is a particularly favorable case for the "α-daughter" method of measuring the counting efficiency. Chemical separations are unnecessary, since both the parent and daughter radiations can be counted in the same sample. The resultant electron-capture counting efficiency was 82 ± 8 per cent.

A prominent γ-ray of 478 ± 10 keV was observed. A number of determinations established the following intensities: *L* X-rays, 65 ± 10 per cent; *K* X-rays, 90 ± 10 per cent, 478 keV γ-ray, 97 ± 10 per cent.

A log *ft* value of 7·4 was calculated[14,22] for electron capture decay to the 478 keV level indicating an allowed hindered or first forbidden unhindered transition. This

* γ-rays of 480 keV and 600 keV were found in preliminary experiments by AMIEL *et al.*[27]

[26] G. H. HIGGINS and K. STREET, JR., *Phys. Rev.* **86**, 252 (1952).
[27] S. AMIEL, R. G. ALBRIDGE, F. S. STEPHENS and F. ASARO. Unpublished data (1957).
[28] L. B. MAGNUSSON, A. M. FRIEDMAN, D. W. ENGELKEMIER, P. R. FIELDS and F. WAGNER, *Phys. Rev.* **102**, 1097 (1956).

is in close agreement with the value given by MOTTELSON and NILSSON[6], who also show a decay scheme indicating decay to an additional level at 640 keV.

The numerous α-pulse analyses of ^{241}Cm gave an α-energy of 5·95 ± 0·02 MeV. This is slightly higher than the previous figure of 5·90 MeV[15]. A total α-branching of 0·96 ± 0·09 per cent, corresponding to a partial α-half-life of 10 ± 1 years, was calculated from these data. The hindrance factor is 2·5 for this α-group, to be compared with values[4] of 1·4 and 2·5 for the α-particle groups in highest abundance of ^{243}Cm and ^{245}Cm respectively.

TABLE 3.—ELECTRON-CAPTURE AND NEGATRON PROPORTIONAL-COUNTING EFFICIENCIES

Isotope	Counting efficiency (on platinum)	Sample mounting method*
Electron capture		
^{234}Np	63[32]	Ev.
^{234}Np	68[32]	V.
^{234}Np	65[32]	Ep.
^{236}Np	89[33]	V.
^{236}Np	95[33]	Ep.
^{237}Pu	77[33]	Ep.
^{239}Am	60†	V.
^{240}Am	90†	Ev., V.
^{241}Cm	82†	V.
Negatron		
Rare earths	78[33]‡	
^{210}Bi	85[34]	
^{238}Np	70[33]	
^{241}Pu	66[34]	

* Ev. refers to samples mounted by evaporation of a carrier-free aqueous solution onto a 2 mil platinum disk followed by heating in a burner to a dull red glow; V. refers to samples volatilized onto a platinum disk from a tantalum filament at ~1800°C *in vacuo*; Ep. refers to samples electroplated onto a platinum disk from neutral ammonium chloride solution (see Reference 32 for further details).

† This paper.

‡ This value is the average for ^{91}Y, ^{95}Zr-^{95}Nb, ^{147}Nd, ^{149}Pm, ^{153}Sm, ^{159}Gd, ^{161}Tb and ^{169}Er.

DISCUSSION

Electron-capture counting efficiencies for the 2π-geometry windowless methane-flow proportional counter (for thin samples mounted on platinum) from the present work and other sources* are summarized in Table 3.

The average counting efficiency for electron capture nuclides included in Table 3 is about 80 per cent, and it is this value that is recommended for use for those nuclides

* Less certain values have been reported for ^{211}At (39 per cent), ^{231}U (33 per cent), ^{243}Bk (26 per cent), and ^{245}Bk (33 per cent) by HULET[29], and for ^{211}At (60 per cent) by HIGGINS[13] and for ^{245}Bk (~100 per cent) and ^{247}Cf (80–90 per cent) by CHETHAM-STRODE and HARVEY[30]. The first set of values, probably much too low, have led to the widespread, but probably erroneous, belief (in connexion with later results) that there is a very wide range of counting efficiencies.

[29] E. K. HULET, Thesis, University of California (1954); Report UCRL-2283 (1953).

[30] A. CHETHAM-STRODE and B. G. HARVEY, Unpublished results (1955).

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for which no direct determination has been made, although caution should be exercised since the counting efficiency depends to some extent on the decay scheme. The high (greater than 50 per cent) counting efficiencies measured for this type of decay in a 2π-geometry windowless proportional counter, and the similarity to the efficiency of the same counter for nuclides which decay by negatron emission should be noted. These high efficiencies can be partly attributed to the backscattering factor[31] on platinum of 1·6 to 1·8 for β-particles (and presumably conversion electrons) of moderate and high energies, but a large contribution to the high counting efficiency must come from Auger electrons and low energy X-rays are usually present in high abundance. An efficiency of 77 per cent has been observed for ^{237}Pu which decays 60[6] per cent to the ground-state of ^{237}Np.

Most of the decay data presented need little further amplification. The preliminary decay schemes of the two odd-odd isotopes, ^{238}Am and ^{240}Am, however, have an unusual and revealing characteristic: essentially all of the electron capture decay leads to levels of about 1000 keV or higher energy. From this observation and inspection of the decay schemes of other odd-odd americium isotopes and odd-odd neptunium isotopes one concludes that it is a general rule that levels >1000 keV must be populated for relatively fast β-decay to even-even plutonium isotopes. The decay of the $\sim$100 year isomer of ^{242}Am (believed to be the ground state[27]) is one case. The decay energy for electron capture is only about 650 keV and the log *ft* value of 12 for decay to the lowest-lying states of ^{242}Pu implies highly forbidden decay.[35] On the other hand, the decay of the 16 hr isomer is characterized by allowed or first forbidden log *ft* values, so the forbiddenness rule may be associated only with decay from ground states. The negatron decay of ^{236}Np, also to an even-even plutonium isotope may be another example of the rule. If the long-lived isomer[36] of ^{236}Np is assumed to be the ground state and the negatron and electron-capture decay energies are assumed to be similar to those noted for the 22 hr isomer of ^{236}Np (which is reasonable from decay-energy systematics[12]) then the log *ft* value is >12 for negatron decay and higher still for electron capture decay. Again the decay from the excited state (22 hr isomer of ^{236}Np) is relatively unforbidden. Among the other beta-minus unstable neptunium isotopes, ^{238}Np exhibits forbidden decay to low-lying levels of ^{238}Pu (log $ft = 8{\cdot}5$ to the 2+ level) and more allowed decay to levels above 1000 keV.[14] The decay of ^{240}Np is apparently similar to that of ^{242}Am and ^{233}Np. The recently assigned 60 min isomer[25] of ^{240}Np (probably the ground state) again decays mainly to excited levels, whereas the 7 min excited state of ^{240}Np undergoes beta transitions[24] to the ground and 560 keV levels of ^{240}Pu with log *ft* values of about 6·5.

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[31] B. P. BURTT, *Nucleonics* **5**, No. 2, 28 (1949).
[32] W. M. GIBSON, Thesis, University of California, (1957); also available as Unpublished Report URCL-3493, (1956).
[33] R. VANDENBOSCH, Unpublished data (1955).
[34] S. G. THOMPSON, A. GHIORSO and B. G. HARVEY, Unpublished data (1955).
[35] R. W. HOFF, H. JAFFE, T. O. PASSELL, F. S. STEPHENS, E. K. HULET and S. G. THOMPSON, *Phys. Rev.* **100**, 1403 (1955).
[36] M. H. STUDIER, J. GINDLER and C. M. STEPHENS, *Phys. Rev.* **97**, 88 (1955).

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THE DETERMINATION OF THE PARTIAL α- AND β-HALF-LIVES OF ^{241}Pu

F. BROWN, G. G. GEORGE, D. E. GREEN and D. E. WATT
Atomic Weapons Research Establishment, Aldermaston, Berkshire

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Abstract—Measurements of α-spectra and α-emission rates from an electromagnetically separated sample of plutonium containing 77% ^{241}Pu gave a value of 13·24 ± 0·24 years for the β-half-life of this isotope and a new value of 5·72 ± 0·1 × 10^5 years for the α-half-life resulting in an α/β branching ratio of 2·31 ± 0·06 × 10^{-5}.

INVESTIGATIONS into the use of ^{241}Pu/^{237}U equilibrium mixtures as possible long-lived standards for ^{237}U produced values for the α- and β-half-lives of ^{241}Pu and hence a value for the α/β branching ratio. Literature values for the α-half-life of ^{241}Pu are variable; THOMPSON *et al.*[1] gave an estimate of 4 × 10^5 years from α-measurements while JONES, *et al.*[2] measured the ^{237}U equilibrium activity and gave a value of 2·9 × 10^5 years. Measurements of the β-half-life are quite consistent. The most satisfactory method is to measure the rate of growth of ^{241}Am, which has been done in two ways. MCKENZIE *et al.*[3] measured the rate of increase of ^{241}Am by α-pulse analyses, applied a correction for the contribution of ^{238}Pu to the ^{241}Am peak, and obtained a value of 13·25 ± 0·2 years, using the value of 461·3 ± 1·7 years[4] for the half-life of ^{241}Am. ROSE and MILSTEAD[5] obtained a value of 12·95 ± 0·28 years by counting the 60 keV γ-ray from ^{241}Am with a xenon-filled proportional counter. Values for the α/β branching ratio vary between 2 and 4·5 × 10^{-5} with a recent value by JENKINS *et al.*[6] of $1{\cdot}9^{-0{\cdot}6}_{+0{\cdot}8}$ × 10^{-5} based on γ-spectrometry. The latter workers used plutonium appreciably enriched (78 per cent) in the ^{241}Pu isotope.

The values for the α- and β-half-lives of ^{241}Pu and hence the α/β branching ratio presented in this paper were obtained on plutonium containing 77% ^{241}Pu. The ^{241}Pu was purified from any ^{241}Am on an ion exchange column. α-pulse analysis of the ^{241}Pu at various times after separation gave the rate of growth of ^{241}Am and the ratio by α-activity of the various nuclides (^{241}Am, ^{241}Pu, ^{239}Pu + ^{240}Pu). A knowledge of the total α-disintegration rate at each of these times and the relative abundances of the plutonium isotopes as determined by mass-spectrometric analysis enabled the the α- and β-half-lives of ^{241}Pu to be calculated.

The chemical purification of ^{241}Pu

The solution of plutonium was evaporated to dryness twice with 0·5 ml of concentrated nitric acid and the residue dissolved in 0·5 ml of concentrated hydrochloric acid. This solution was transferred to a column of Amberlite XE 119 anion exchange resin conditioned with concentrated hydrochloric acid, and the ^{241}Am eluted by washing with 0·5 ml portions of concentrated hydrochloric

[1] S. G. THOMPSON, K. STREET, A. GHIORSO and F. L. REYNOLDS, *Phys. Rev.* **80**, 1108 (1950).
[2] J. P. BUTLER, T. A. EASTWOOD, R. P. SCHUMAN and M. E. JONES, KAPL 1378 (1955).
[3] D. R. MCKENZIE, M. LOUNSBURY and A. W. BOYD, *Phys. Rev.* **90**, 327 (1953).
[4] G. R. HALL and T. L. MARKINS, *J. Inorg. Nucl. Chem.* **2**, 202 (1956).
[5] B. ROSE and J. MILSTEAD, *J. Nucl. Energy*. **2**, 264 (1956)
[6] H. M. DAVIS, G. W. C. MILNER, F. J. W. GARTON, H. I. SHALGOSKY and E. N. JENKINS, *Progress in Nuclear Energy* Series 9, *Analytical Chemistry* Vol. I, p. 5. Pergamon Press, London (1959).

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acid until 6 ml of effluent were collected. The time of the last wash was taken as the plutonium/americium separation time. The column was then filled with concentrated hydrochloric acid containing 1 per cent hydrochloric acid (s.g. 1·94) and allowed to stand for 20 min to ensure reduction of plutonium to the trivalent state; the plutonium was then eluted from the resin by washing with 6 ml of the hydrochloric/hydriodic acid mixture in 0·5 ml portions. The effluent was evaporated to dryness and re-evaporated with concentrated nitric acid to remove iodine and reoxidize the plutonium. The residue was dissolved in 4 M nitric acid and the plutonium extracted with methyl-isobutyl-ketone. Sources for α-pulse analysis were made by direct evaporation of aliquots of the ketone solution on stainless steel disks.

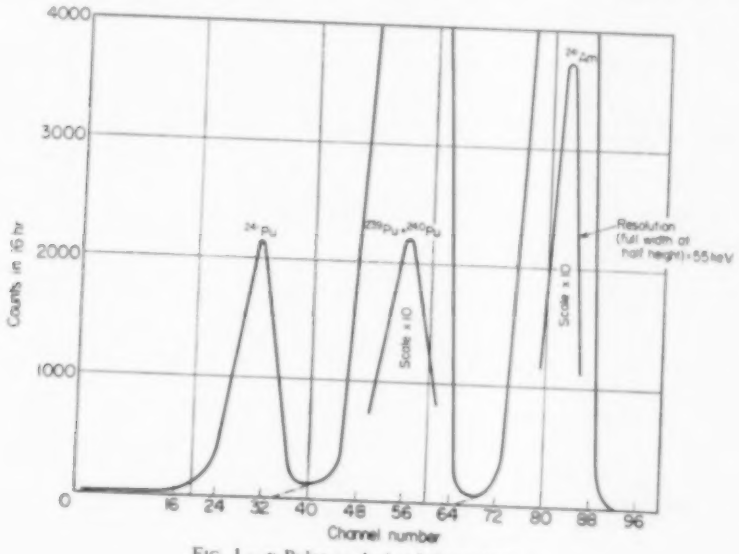

FIG. 1.—α-Pulse analysis of plutonium.

The determination of the α-half-life of ^{241}Pu

As several months had elapsed since the plutonium had been electromagnetically separated in HERMES, two samples were purified from ^{241}Am and the isotopic composition of the plutonium measured mass-spectrometrically; the values obtained were 17·97 ± 0·2% ^{239}Pu, 5·51 ± 0·01% ^{240}Pu, and 76·52 ± 0·2% ^{241}Pu. No ^{242}Pu was detected.

A source of approximately 10^6 α-disintegrations per min of this plutonium on a stainless steel disk was examined in a low-geometry proportional counter with a time constant of 100 μ sec. With a counting rate of the order of 60 counts/min coincidence losses were negligible. Methane purified by freezing in liquid nitrogen, was used as the counting gas and pulses from the counter were amplitude sorted. Three types of pulse height analyser were used as available: results from each were in excellent agreement. The counter background in the energy range 4·0–6·1 MeV was 5 counts/hr. Fig. 1 shows a typical specimen. Possible methods of interpreting the "tail" of each peak are:—

(a) That obtained when kicksorting a monoenergetic α-emitter;

(b) That expected from the thickest source that can possibly fit the measured peak shapes;

(c) That obtained by extrapolation of the slope on the low energy side of the peak.

In the calculations it is assumed that the "tails" have shape (a), which introduces a maximum error of 1 per cent in the measurement of the number of counts in each peak. A source was counted regularly over a period of three months. The counter was refilled with gas before each run and the overall drift of the instrument and associated electronics during each run was negligible. The results obtained over this period are shown in Table 1.

Immediately before and after some of the runs in the low-geometry counter the absolute α-count of the source was determined on a scintillation counter of known efficiency. From the average of each pair of α-scintillation counts and the appropriate ratio of the nuclides from the α-pulse analysis,

it was possible to determine the disintegration rate of ^{241}Am (Table 1) and hence the total α-disintegration rate due to plutonium.

From the ratio (^{241}Pu)/(total Pu) of 7·83 ± 0·03 per cent, determined by α-pulse analysis (Table 1), the total disintegration rate of 3·202 ± 0·006 × 10^4 due to plutonium on the source (Table 1) and the relative abundances of the plutonium isotopes, the α-half-life of ^{241}Pu is calculated to be 5·72 ± 0·12 × 10^5 years, using half lives[7] of 2·44 × 10^4 years and 6·60 × 10^3 years for ^{239}Pu and ^{240}Pu respectively.

TABLE 1

Total α (disintegrations/min)	$\frac{^{241}\text{Am}}{\text{Total}}$	$\frac{^{241}\text{Am}}{^{241}\text{Pu}}$	$\frac{^{241}\text{Pu}}{\text{Total Pu}}$	Total Pu (disintegrations/min)
3·575 × 10^4	10·25	150·6	7·79	3·208 × 10^4
4·496	28·76	524·6	7·70	3·203
4·843	33·60	639·0	7·92	3·216
4·886	34·43	675·0	7·78	3·204
5·783	44·60	1045	7·69	3·204
6·061	46·90	1128	7·85	3·218
6·402	49·80	1263	7·85	3·214
6·632	52·40	1397	7·89	3·157
7·020	54·30	1484	8·08	3·208
7·315	56·40	1652	7·88	3·190

The figures in columns 2, 3 and 4 are per cent by alpha activity.
From Table 1 the average values for the total disintegration/min of plutonium and the ^{241}Pu/total Pu are 3·202 ± 0·006 × 10^4 and 7·83 ± 0·03 per cent respectively.

A repeat experiment on a second source gave 7·84 ± 0·04 per cent and 1·055 ± 0·012 × 10^5 disintegration/min for the corresponding values and hence a value for the half-life of 5·71 ± 0·15 × 10^5 years.

The overall value for the α-half-life of ^{241}Pu is therefore 5·72 ± 0·10 × 10^5 years.

The determination of the β-half-life of ^{241}Pu

The β-half-life can be calculated from the rate of growth of ^{241}Am. Using the data presented in Table 1, it is possible to obtain the disintegration rates of ^{241}Am, of total plutonium, and hence of ^{241}Pu as a function of time from the initial Am/Pu separation. The ratio R, (α-disintegration rate of ^{241}Am)/(α-disintegration rate of ^{241}Pu), is calculated and a plot of R vs. time from the americium/plutonium separation (Fig. 2) made. Using the slope of this curve, the value of 461·3 ± 1·7 years for the half-life of ^{241}Am,[4] and the values for the α-half-life of ^{241}Pu previously measured, the two sources give 13·17 ± 0·31 years and 13·30 ± 0·36 years for the β-half-life of ^{241}Pu. The mean of these is 13·24 ± 0·24 years.

The α/β branching ratio

Using figures of 5·72 ± 0·1 × 10^5 years and 13·24 ± 0·24 years for the α- and β-half-lives respectively, the value of the branching ratio is 2·31 ± 0·06 × 10^5.

[7] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, (2) 823, Part 2 (1958).

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DISCUSSION

Data accumulated during this work gave a value of $5{\cdot}72 \pm 0{\cdot}1 \times 10^5$ years for the α-half-life of ^{241}Pu, in excellent agreement with that predicted for ^{241}Pu by PERLMAN[8] from α-decay systematics. As an additional check on the accuracy of the half-life, essentially the same data was used to calculate the β-half-life of ^{241}Pu. This gives a value of $13{\cdot}24 \pm 0{\cdot}24$ years and is in good agreement with values quoted in the literature. The standard deviation on these results takes into account the

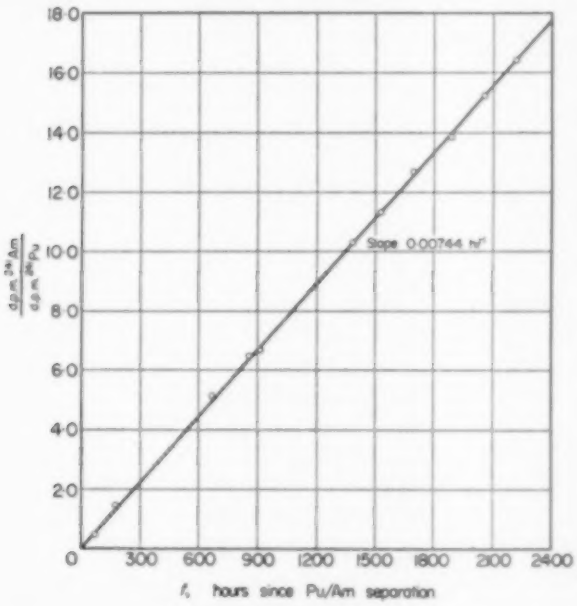

FIG. 2.—Growth of ^{241}Am in ^{241}Pu.

uncertainties in the quoted half-lives of ^{239}Pu, ^{240}Pu and ^{241}Am. Finally, the value of $2{\cdot}31 \pm 0{\cdot}06 \times 10^{-5}$ for the α/β branching ratio lies well within the limits of $1{\cdot}9^{-0{\cdot}6}_{+0{\cdot}8} \times 10^{-5}$ obtained by JENKINS *et al.*[6]

The value of 4×10^5 years[1] quoted for the α-half-life does not appear to have been corrected for α-contributions due to ^{242}Pu in the samples while the value of $2{\cdot}9 \pm 0{\cdot}5 \times 10^5$ given by GIFT[2] depends on a considerable number of corrections and calibrations on a sample of low ^{241}Pu content.

On the basis that the present work involves a minimum of corrections and has an unambiguous interpretation, the α-half-life is considered to be more accurate than previously determined values.

Acknowledgements—We wish to thank Mrs. R. C. JEFFEREY for the mass-spectrometric analyses, and Dr. F. MORGAN for his interest in this work. The ^{241}Pu was supplied by A.E.R.E., Harwell.

[8] I. PERLMAN, A. GHIORSE and G. T. SEABORG, *Phys. Rev.* **77**, (26) (1950).

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 196 to 199. Pergamon Press Ltd. Printed in Northern Ireland

NEW ISOMERS OF SCANDIUM-50 AND INDIUM-120; γ-RAYS IN LUTECIUM-178 DECAY*

A. POULARIKAS, J. CUNNINGHAM,† W. MCMILLAN,‡
J. MCMILLAN and R. W. FINK§
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas

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Abstract—In the course of a systematic study of fast neutron activation cross-sections utilizing the Arkansas 400 kV Cockcroft–Walton accelerator, several new radioactive species have been identified and γ-rays assigned in the decay of others. In addition, several unidentified new radioactivities have been observed, but not studied further. What follows below is a summary of all our available new information on these activities.

NEW ISOMER OF ^{50}Sc

WHILE investigating 14·8 MeV neutron activation cross-sections of titanium[1] on the Arkansas 400 kV Cockcroft–Walton accelerator, a new activity appeared in the gross β-decay curves (Fig. 1) with a half-life of 23 ± 3 min. A methane-flow, 0·9 mg/cm aluminized-mylar end-window β-proportional counter was used. The 23 min activity was observed in all bombardments of natural titanium foils¶ and of 84·69 per cent enriched ^{50}Ti oxide, but not from irradiations of 85·6 per cent enriched ^{47}Ti or 81·5 per cent enriched ^{49}Ti oxide containing 1·4% ^{50}Ti. It therefore can be assigned to mass number 50. Radiochemical separation described below definitely assigns the new 23 min period to ^{50}Sc. Previously a 1·5 min activity, formed by the ^{50}Ti (n,p) reaction with cyclotron-produced Be-d neutrons, has been assigned to ^{50}Sc by MORINAGA and BLEULER.[2] We confirm this observation[1] of the 1·5 min period induced by 14·8 MeV neutrons in natural titanium and in enriched ^{50}Ti oxide, but because of its short half-life we could not perform a radiochemical separation of it.

From natural titanium foils after irradiation a new γ-ray of 493 ± 30 keV was observed with a high counting rate on a 3×3 in. NaI(Tl) scintillation spectrometer and 50-channel analyser and with a $1\frac{1}{2} \times 1$ in. NaI(Tl) single-channel spectrometer with manual scaler. The gamma photopeak decayed with a 23 min half-life and so is assigned to the new ^{50}Sc isomer.

The radiochemical procedure used to establish the 23 min activity as belonging to scandium involved the use of a recent method for the sharp separation of scandium, titanium, and vanadium by anion exchange.[3] About 50 mg of bombarded natural titanium foil was dissolved in concentrated HF with heat. H_2O_2 was added and the

* Supported in part by the U.S. Atomic Energy Commission.
† Present address: Argonne National Laboratory, Lemont, Illinois.
‡ Department of Physics.
§ Present address: Gustaf Werner Institute for Nuclear Chemistry, Univ. of Uppsala, Sweden.
¶ Spectroscopic analysis supplied by American Silver Co., Flushing, N.Y., list impurities in the natural titanium foils as follows: C, 0·018; Fe, 0·05; N, 0·01; H, 0·007%.

[1] A. POULARIKAS and R. W. FINK, *Phys. Rev.* In press.
[2] H. MORINAGA and E. BLEULER, *Phys. Rev.* **100**, 123 A (1955); *Bull. Amer. Phys. Soc.* **30**, No. 7, 9, A 2 (1955).
[3] U. SCHINDEWOLF and J. W. IRVINE, JR., *Analyt. Chem.* **30**, 906 (1958).

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solution diluted to 1 M in HF and passed through a column of Dowex-1 in the fluoride form; scandium, titanium, and vanadium are absorbed.[3] Several column volumes of 2·5 M HF were passed through, since this eluant removes vanadium, followed by three to five column volumes of 15 M HF. This has been shown[3] to separate scandium cleanly. Evaporation and counting of the 15 M HF fraction revealed the 23 min activity together with other known scandium activities (Fig. 1). Recovery of carrier-free scandium was low (5–10 per cent), but could be increased to 30–40 per cent by addition of about 5 mg scandium carrier to the original concentrated HF solution of the target.

Colorimetric determinations of titanium present in the 15 M HF eluted scandium fraction were made using the peroxy colour produced by H_2O_2. In order to obtain true, stable colours, it was found necessary to evaporate the test portion of eluant to dryness with H_2SO_4 to expel fluoride and to use Be^{2+} in the colorimetric solutions to prevent interference by residual fluoride.[4]

Decontamination factors of titanium from scandium normally ranged from 100 to 500 for separations completed in 20–30 min. These could be improved, but at excessive increase of the time required, by a second absorption–desorption cycle or by increasing the column length.

A further independent chemical identification of the 23 min activity as scandium was carried out as follows: Solutions of irradiated titanium in hot, concentrated HF were added to concentrated H_2SO_4 in a Pyrex vessel with quartz chips present to facilitate the total expulsion on heating of fluoride as H_2SiF_6. After heating and dilution, a test portion of this solution gave no visible precipitate with dilute HF, so lanthanum carrier was added and LaF_3 precipitated. The 23 min activity was clearly resolved from the other known scandium activities carried down with LaF_3. The known titanium activities were identified in a precipitate subsequently obtained on addition of NaOH to the decanted liquid.

^{120}In ISOMERS

Two activities having half-lives of $3{\cdot}0 \pm 0{\cdot}8$ sec and 50 ± 1 sec were observed in bombardments of highly-enriched ^{120}Sn samples with 14·8 MeV neutrons. The 50 sec activity exhibits a maximum β-energy $E_{\beta^-} = 2{\cdot}2 \pm 0{\cdot}4$ MeV, measured with a plastic crystal scintillation-spectrometer with 50-channel analyser, and γ-rays of $0{\cdot}73 \pm 0{\cdot}03$, $0{\cdot}85 \pm 0{\cdot}03$, $1{\cdot}02 \pm 0{\cdot}01$, and $1{\cdot}18 \pm 0{\cdot}01$ MeV, based on studies using a 3×3 in. NaI(Tl) scintillation spectrometer with 50-channel analyser. The 1·02 and 1·18 MeV gammas arise from known transitions[5] from levels in ^{120}Sn and therefore serve as additional evidence that the 50 sec activity is an isomer of ^{120}In. Previously a 55 sec half-life was reported by McGinnis,[6] who bombarded natural tin with 20 MeV neutrons. The cross-section for the ^{120}Sn$(n,p)^{120m}$In (50 sec) reaction at 14·8 MeV was found to be $2{\cdot}8 \pm 1{\cdot}0$ millibarns.

Because the 3·0 sec activity was observed in cross-bombardments of highly enriched ^{120}Sn, natural tin, and natural antimony, it can be assigned definitely to ^{120}In. It is a hard β-emitter, but its radiation characteristics have not been studied otherwise. It is formed in the ^{120}Sn(n,p) reaction with a cross-section of approximately 1 millibarn at 14·8 MeV.

[4] F. Fiegl and A. Schaeffer, *Analyt. Chem.* **23**, 353 (1951).
[5] *Nuclear Data Cards*, National Research Council, Washington, D.C.
[6] C. L. McGinnis, *Phys. Rev.* **109**, 888 (1958).

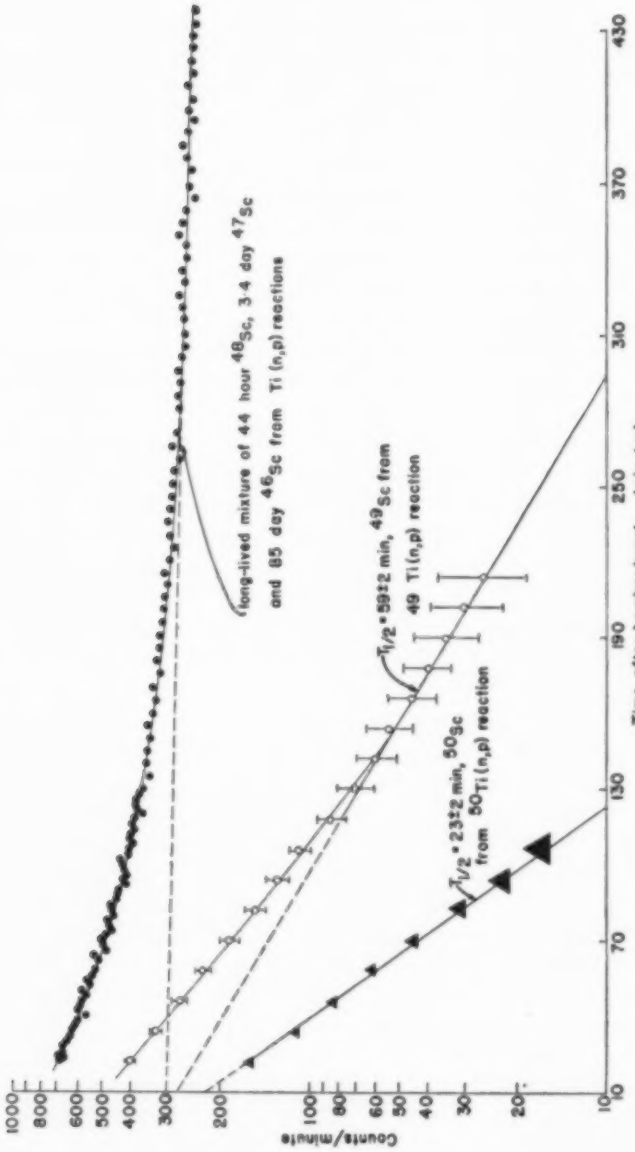

FIG. 1.—Typical gross β-decay curve obtained from the scandium fraction radiochemically separated from natural titanium targets. The new 23 min activity was observed also in irradiations of enriched $^{50}TiO_2$ and natural titanium without chemical separation along with the known 1·5 min ^{50}Sc isomer, but was not observed from enriched $^{49}TiO_2$ on enriched $^{47}TiO_2$.

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OTHER ACTIVITIES OBSERVED

From irradiations with 14·8 MeV neutrons of natural cadmium, a 4·5 sec activity was observed; recently, it has been radiochemically identified[7] as ^{114}Ag in uranium fission. New half-lives of 2·3 sec from natural molybdenum and 3·6 sec from natural palladium were found in 14·8 MeV neutron bombardments but have not been identified. From 93·7 per cent enriched ^{116}Cd bombardment, 1·5 min ^{113}Pd was produced by the (n,α) reaction, which confirms the otherwise known mass assignment.[5]

22·0 MIN ^{178}Lu

In the course of measuring 14·8 MeV neutron activation cross-sections of tantalum, radioactive ^{178}Lu was studied from the ^{181}Ta(n,α) reaction. A new value of the half-life was measured and found to be 22·0 ± 0·5 min. γ-rays of 327 ± 15, 434 ± 15, 560 ± 30, 674 ± 30, and 780 ± 30 keV, each of which decayed with a 22 min half-life, were observed with a 3 × 3 in. NaI(Tl) scintillation spectrometer and 50-channel analyser using the successive peeling off method described previously.[8] Previously gammas at 342 ± 3, 445 ± 5, and 550 (very weak) keV were reported to decay with a 19–20 min half-life.[9] In the gamma spectrum, a peak at 523 ± 30 keV was found to decay with approximately a 10 min half-life. This new activity does not appear to be due to an impurity in the tantalum foil, but it remains so far unidentified.

The activation cross-section for the ^{181}Ta$(n,2n)^{180m}$Ta (8·0 hr) reaction was measured at 14·8 MeV giving a value of 2740 ± 30 millibarns, based on the ^{63}Cu$(n,2n)^{62}$Cu monitoring reaction (556 millibarns). An absolute value of 2640 ± 200 millibarns at 14·1 MeV has been reported[10] from experiments in which neutrons were counted in a 240 gallon cadmium-loaded liquid scintillator. It is evident from a comparison of the activation cross-section with the total $(n,2n)$ cross-section that the 8·0 hr isomeric state is formed essentially exclusively with very little production of the ^{180}Ta ground-state at this bombarding energy.

Acknowledgement—We are indebted to Mr. J. E. Wray of the Accelerator Laboratory for assistance with the bombardments.

[7] J. M. Alexander, U. Schindewolf and C. D. Corvell, *Phys. Rev.* **111**, 228 (1958).
[8] W. C. Beggs, B. L. Robinson and R. W. Fink, *Phys. Rev.* **101**, 149 (1956).
[9] von Th. Stribel, *Z. Naturf.* **12** A, 519 (1957)
[10] V. J. Ashby, H. C. Catron, L. L. Newkirk and C. J. Taylor, *Phys. Rev.* **111**, 616 (1958).

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 200 to 211. Pergamon Press Ltd. Printed in Northern Ireland

CHEMICAL EFFECTS OF RADIATIVE NEUTRON CAPTURE IN $CrEn_3Br_3$

A. TURCO
Centro Chimica Nucleare C.N.R., Università, Padova, Italy

(*Received* 20 *July* 1959)

Abstract—The complex compound tris-ethylenediamine chromium (III) bromide was irradiated with neutrons in B.E.P.O. at Harwell. Depending on the conditions of irradiation, 5–40 per cent of the activity was found on precipitation on lead chromate from aqueous solutions of the irradiated compound. On further separation using ion exchange columns and electrophoresis, it was shown that this activity was due to ^{51}Cr not in the form of chromate, but in an unidentified species which co-precipitates with lead chromate. By exposing the irradiated sample to a source of γ-rays it was shown that this unknown species is formed by γ-annealing in the reactor. The significance of the patterns of electrophoretic separation is discussed and the peaks are tentatively identified.

Under the condition of this investigation, no evidence was obtained for an internal γ-conversion effect for ^{51}Cr.

THIS work is related to a previous investigation of the possibility of the formation of hexavalent chromium, following the neutron irradiation of chromic compounds.[1] Slow neutron irradiation of chromic salts (e.g. the sulphate, nitrate, alum) in the solid state was repeatedly shown to lead to the formation of variable amounts (5–10%) of chromium-51 in the form of chromate;[2] similar results had been found working with aqueous solutions of chromic salts.[3] The possibility of an oxidation through internal conversion of the neutron capture γ-radiation obviously had to be taken into consideration.[4]

On the basis of these results, it was decided to investigate the Szilard effect on the complex compound $CrEn_3(NO_3)_3$.[1] The following results were found with samples irradiated at very low pile factors ($< 0{\cdot}1$); activity on Cr(III) 39 per cent, activity on Cr(VI) 6 per cent, residual activity 56 per cent.

The method of analysis used involved precipitation of the Cr(VI) on lead chromate, followed by precipitation of the chromic ions as chromic hydroxide.

Apparently those figures indicated that bond breaking through the recoil mechanism is far more important than γ-conversion in disrupting the original molecules, but they did not exclude the possibility that internal conversion of γ-rays may be partly responsible for bond breaking. Nevertheless the 6 per cent of oxidized radioactive chromium was supposed to define an upper limit for the last mechanism, because the crystalline matrix could be considered a substantially oxidizing medium, owing to the presence of nitrate groups.

The present work deals with the results obtained in similar experiments on $CrEn_3Br_3 \cdot 4H_2O$.

[1] A. TURCO and M. SCATENA, *Ricerca Sci.* **25**, 2651 (1955).
[2] G. HARBOTTLE, *J. Chem. Phys.* **22**, 1083 (1954).
[3] L. M. FISHMAN and G. HARBOTTLE, *J. Chem. Phys.* **22**, 1088 (1954).
[4] A. G. MADDOCK and M. M. DE MAINE, *Canad. J. Chem.* **34**, 441 (1956) and references quoted therein.

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EXPERIMENTAL

Preparation of pure chromium salts. Reagent dichromate was passed through a cation exchanger to get rid of cationic impurities. Barium chromate was precipitated, sulphuric acid added and after filtration the chromic acid reduced with ethyl alcohol. Chromium sulphate was crystallized from the solution. As a test of radiochemical purity, comparison of the 0·32 MeV γ-radiation spectrum with that of an irradiated sample of spectroscopically pure Cr_2O_3 showed no impurities. The compounds $CrEn_3Br_3 \cdot 4H_2O$, $[CrEn_2(H_2O)Br]Br_2$ and $[CrEn_2(H_2O)_2]Br_3$ were prepared by the method of PFEIFFER[5].

Absence of isotopic exchange between CrO_4^{2-}, $CrEn_3^{3+}$, $Cr(H_2O)_6^{3+}$. It was known that $CrEn_3(NO_3)_3$ does not exchange with chromate or chromic ions. The influence of bromide was studied in both exchange systems. No exchange was found.

Tests for decomposition of $CrEn_3^{3+}$. The tests for photochemical decomposition of the aqueous solution during samples handling, and by radiation damage were made by looking for changes in the visible absorption spectra. A decomposition of less than 4 per cent was observed.

Bombardments. Bombardments were made with neutrons in B.E.P.O. at Harwell. All bombardments were made in the presence of air, the samples being contained in plastic ampoules. All samples were permitted to stand at least 20 days before measurement to allow the bromine radioactivity to decay.

Separation procedures. Three types of separation were used. The chemical separation method involved addition of chromic and chromate ions as carriers and precipitation of lead chromate and chromic hydroxide as outlined above.[1] A second precipitation showed the completeness of carrying on the first. The individual precipitates were transformed into standard chromic chloride solutions and counted in polyethylene cells with a γ-scintillation counter.

In other experiments a column of Dowex 50 resin was used to eliminate all cationic species from the solution; blank runs had previously shown that only 1 per cent of chromate is reduced to chromic ion when the resin is pre-treated with chromate solution. Colloidal species may also have been removed in this treatment.

Electrophoresis was finally used to identify the species formed in recoil. Samples of the irradiated compounds were dissolved in various media at a concentration of 10–20 mg/ml. Portions of 10–20λ were placed at the zero line on the electrophoresis strip (Whatman No. 3 paper). Potentials of the order of 350–600 V were applied, the useful length of the strips being about 30 cm. The strips were cooled during electrophoresis by immersion in carbon tetrachloride.[6] After 2–3 hr the voltage was interrupted, the paper dried and cut transversely in 1 cm strips. These were scintillation-counted in a standard way.

RESULTS AND DISCUSSION

Using the chromate and chromic hydroxide precipitation method of separation the following results were obtained.

The percentage of radio-chromium entered in the tables under "retention" was obtained by measuring the activity still present in the solution after precipitation as $PbCrO_4$ and $Cr(OH)_3$. The residual chromium remaining in solution after this treatment was not necessarily in the form of $CrEn_3^{3+}$, but could have been in any related species (containing less than three molecules of ethylenediamine) from which chromium cannot be precipitated by the above procedure.

The order followed in the experiments was the following. The first experiments made were (1) and (5). These results threw some doubt on the hypothesis that hexavalent radioactive chromium was formed by gamma internal conversion. Clearly if this were the case the percentage of oxidized radio-chromium should not depend on the pile factor.

The results of the annealing experiments contained in Table 1 [Experiments (3),

[5] P. PFEIFFER, *Ber. Dtsch. Chem. Ges.* **40**, 3828 (1907).
[6] J. D. SMITH and M. MARHAM, *Nature, Lond.* **168**, 406 (1952).

(4)] and Table 2, show an evident increase in the activity of the lead chromate, accompanied by a corresponding decrease of activity on the chromic hydroxide. No meaning may be attributed to the small variations in retention, because this is so small that its experimental determination, following the separation method which was used, may be considerably influenced by small errors in the separation of $PbCrO_4$ and $Cr(OH)_3$; nevertheless it may be concluded that reformation of the original molecule is a very improbable process because the retention always remains very small. These results were interpreted in the following way.

TABLE 1.—PERCENTAGE DISTRIBUTION OF RADIOACTIVITY ON $PbCrO_4$, $Cr(OH)_3$ AND $CrEn_3Br_3$

Sample*	1	2	3	4	5
Cr(VI)	7·8–7·3	6·1	20	38	38–41
Cr(III)	87·2–86·4	89	68	55	52–53
"Retention"	4·8–6·3	5	12	7	7–10

* Treatment of samples. (1) Irradiation at p.f. 0·1 for one week; sample investigated 50 days after irradiation. (2) Irradiation at p.f. 0·1 for two weeks; sample investigated 30 days after irradiation. (3) Sample (2) plus 11 Mrad from ^{60}Co source. (4) Sample (2) plus 15 Mrad from ^{60}Co source. (5) Irradiation at p.f. 1·0 one week; sample investigated 20 days after irradiation. (Pile factor, p.f. 1 = 10^{11} neutrons cm^2/sec^{-1}).

TABLE 2.—EFFECT OF HEATING AT 80°C ON SAMPLE (5) 40 DAYS AFTER IRRADIATION

Hours of heating	0	1	3	6	25
Cr(VI)	45	47	55	70	71
Cr(III)	—	47	41	25	21
"Retention"	—	5	3	5	8

Chromium(VI) could arise from some precursor by oxidation either with atomic oxygen or, less likely, by atomic bromine, both of which are probably released in the course of the irradiation.

Alternatively some unidentified, possibly cationic compound containing Cr(III)–ethylenediamine and perhaps bromine ions, could have been formed by annealing from the fragments of disrupted molecules and was co-precipitated (or scavenged in a similar way) on the lead chromate.

Ion exchange experiments

Solutions of the irradiated samples (chromic nitrate and potassium chromate were added as carriers), were passed through a short column of Dowex 50 resin; chromic nitrate was again added to the eluate and lead chromate precipitated following the usual procedure. In this case only 1 per cent of the activity was collected on the precipitated lead chromate. This result confirmed the absence of an appreciable percentage of radioactive chromium as chromate in the solution of the irradiated salt. Thus the species codepositing on the lead chromate is cationic.

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Effect of γ-rays

Comparison of the results of Experiments (1) and (2) with those of Experiment (5) could be interpreted in the following way: the γ-background in the reactor is responsible for the formation of the unknown species which precipitates with lead chromate; the γ-flux may be roughly estimated as proportional to the neutron flux. This explains the fact that with higher pile factors a greater proportion of the activity is precipitated on the lead chromate. Experiments (3) and (4) gave a clear evidence of this fact.

Electrophoresis results

It was thought that electrophoretic separations might clarify this situation. First of all, samples of possible products were prepared and subjected to electrophoresis under standard conditions. These compounds were the following: $CrEn_3Br_3$, CrO_4^{2-}, $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(Cl,Br)]^{2+}$, $[CrEn_2(H_2O)_2]^{3+}$, $[CrEn_2Br(H_2O)]^{2+}$; the last compound was not taken in consideration further after kinetic experiments had shown that the hydrolysis reaction

$$[CrEn_2Br(H_2O)]^{2+} + H_2O \rightleftarrows [CrEn_2(H_2O)_2]^{3+} + Br^-$$

takes place in a few minutes at room temperature; as expected the first aquation step starting from $[CrEn_2Br_2]^+$ is still faster. Unfortunately we did not find described in the literature suitable compounds containing only one ethylenediamine molecule.

No detectable amount of activity was ever found in the anodic zone of the electrophoresis strips, thus confirming the absence of radioactive chromate. In typical runs the distribution of the compounds examined was the following (perchloric acid medium): $[Cr(H_2O)_5(Cl,Br)]^{2+}$ 15–20 cm, $CrEn_3^{3+}$ 24–25 cm, $[CrEn_2(H_2O)_2]^{3+}$ 24·5–25·5 cm, $[Cr(H_2O)_6]^{3+}$ 24–26 cm.

Experiments were made in various solutions and at pH values between two and eleven. For brevity only the patterns which are necessary for the discussion are reported here. Figs. 1–9 show the results in perchloric medium, Figs. 10 and 11 refer to the electrophoresis pattern in hydrochloric acid medium. For the discussion the electrophoresis patterns have been divided into three zones: 20–25 cm, 15–20 cm, 0–15 cm.

(1) Fig. 8 shows that in neutral medium aquochromium species do not move far. The small diffusion movement may arise from a true electrophoretic effect on the chromic hydroxide particles. Peaks of Fig. 4 and Fig. 6 in the 20–25 cm region are consequently given by $CrEn_3^{3+}$ and/or $[CrEn_2(H_2O)_2]^{3+}$ species. It is difficult to decide between them because they have practically the same mobility. Nevertheless we are more inclined to attribute most of the activity of this zone to $[CrEn_2(H_2O)_2]^{3+}$ species, considering that, as is clearly seen from Figs. 2, 4 and 6, the peak under discussion only appears when the sample receives a large dose of γ-rays; we believe that recombination of fragments should lead first to the formation of simpler $CrEn_2^{3+}$ groups.

An important conclusion may be drawn from Fig. 2. With samples irradiated at low pile factors, i.e. when the γ-flux is comparatively less important, no activity is found in this region, thus showing that practically all neutron-capture events lead to disruption of the molecules. At pH 2 the $[Cr(H_2O)_6]^{3+}$ peak superimposes the $CrEn_3^{3+}$ peak.

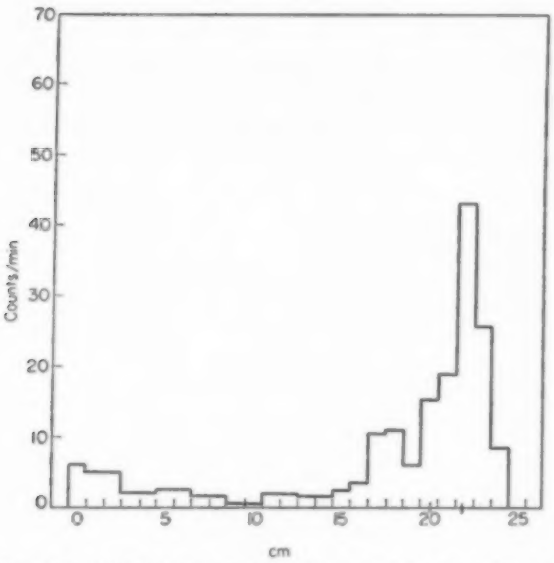

FIG.* 1.—Sample irradiated for one week at pile factor 0·1. Electrolyte: 0·2 M $NaClO_4$, 0·01 M $HClO_4$.

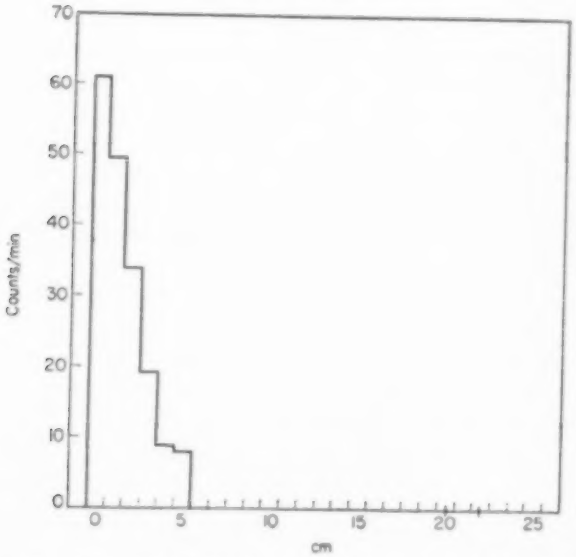

FIG. 2.—Sample irradiated as in Fig. 1. Electrolyte: 0·2 M $NaClO_4$.

* Figs. 1–11.—Electrophoresis patterns. The zero point is the starting line; voltage was applied in such a way that positive ions move to the right. The two parallel lines marked on the cm-axis in the 20–25 cm zone, indicate position of the yellow spot of $CrEn_3^{3+}$, which was used as a reference point.

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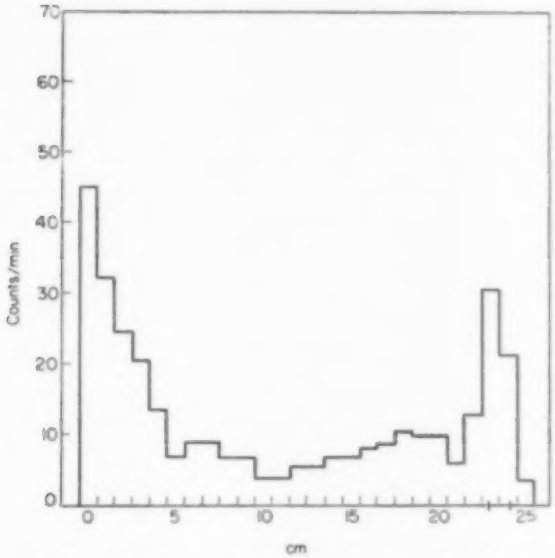

FIG. 3.—Sample as for Fig. 1 and Fig. 2, irradiated for one week at p.f. 0·1 and subsequently subjected to gamma irradiation (15 Mrad from ^{60}Co source). Electrolyte: 0·2 M $NaClO_4$, 0·01 M $HClO_4$.

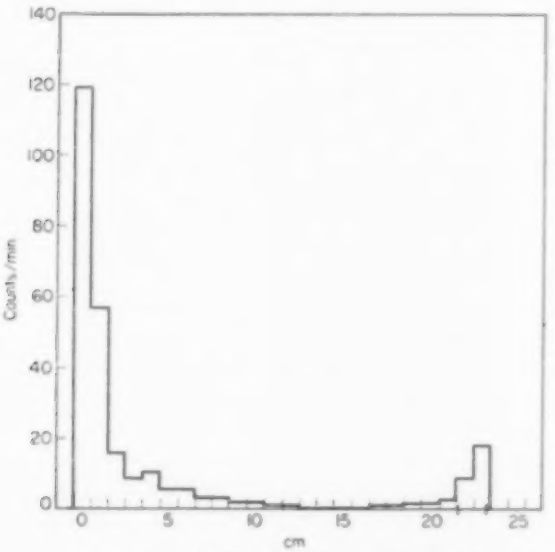

FIG. 4.—As for Fig. 3. Electrolyte 0·2 M $NaClO_4$.

(2) Fig. 7 refers to electrophoresis of a solution of aquochromic ions obtained reducing radioactive chromate in slightly acidic hydrobromic acid solution, to which some drops of ethanol had been added. Since the peak at 25 cm belongs to $[Cr(H_2O)_6]^{3+}$, it may be argued (even from the green colour of the solution) that the peak between 15 and 20 cm belongs to $[Cr(H_2O)_5Br]^{2+}$.

Comparing Figs. 1, 3, 5 and 7, one might attribute the 15–20 cm peak to this last compound. Actually the identity of this peak is rather doubtful. It could easily be a cation containing two or possibly one molecule of ethylenediamine and one halogen atom, with a net charge +2; we think that the evidence suggests that the charge is +2, but unless it is known that one or both of the En complexes would resist hydrolysis at pH 7 (the electrophoresis conditions), they cannot be excluded. In fact increase of pH frequently converts the 15–20 cm peak species into charged but very slow moving species (5–15 cm Figs. 4 and 6) while Fig. 8 shows that aquochromium compounds are not found beyond 5 cm in the same conditions; these may be polynuclear species involving En complex cations.

It was hoped at this point, that electrophoresis of solutions from which all aquochromium species had been eliminated by precipitation as $Cr(OH)_3$ could give evidence in favour of this supposition. The results are shown in Fig. 9. Qualitative evidence seems to be in favour of the hypothesis of $[CrEn_2(\ )]^{2+}$ species, since the peak at 15–20 cm is still present after elimination of the aquochromium species.

To make a quantitative comparison of the results summarized in Fig. 5 and Fig. 9 (where the experimental conditions are the same except for the removal of aquochromium ions in one case), it is necessary to correct the percentages in Fig. 9 to allow for the activity which was removed on chromium hydroxide. When this correction is made (see Fig. 9 for details) the activity of the 20–25 cm peak is 16 per cent which agrees well with the 17 per cent in Fig. 6, confirming the elimination of the $[Cr(H_2O)_6]^{3+}$ species. An activity of 9 per cent is still found in the 15–20 cm peak (instead of 21 per cent of Fig. 5) and this shows that another ion as well as possibly $[Cr(H_2O)_5Br]^{2+}$ must be present in the 15–20 cm peak of Fig. 5.

However it is rather surprising that this unknown species does not appear in the same form at pH 7 (Fig. 6). It seems that while it can resist hydrolysis at pH 8–9 during the precipitation of $Cr(OH)_3$ it is completely decomposed during electrophoresis at pH 7, the higher temperature under the conditions of electrophoretic separation being perhaps the determining factor.

(3) No simple hypothesis can be made as to the nature of the radioactive species occupying the 0–15 cm zone in the histograms in acid medium. They are probably relatively low charged species of large size. Some of them appear to have zero charge (0–5 cm) other could be polynuclear chromium–ethylenediamine complex ions (5–10 cm). Compounds of both types are known to exist. As examples of non-electrolyte complexes one can give the compounds of the series $[Cr(H_2O)Am_2R_3]$: compounds are known with Am = NH_3 and R = SCN, OH, or with Am = pyridine and R = F, Cl, OH; the two molecules of monoacid base could well be substituted by one molecule of ethylenediamine. As an example of known polynuclear complex the compound $\{Cr[(OH)_2CrEn_2]_3\}^{6+}$ could be taken.

The complexity and the great number of the possible species can easily explain the low resolution of the histogram in this zone. Besides, it is also possible that some of these are labile species. Actually 24 hr standing at room temperature in

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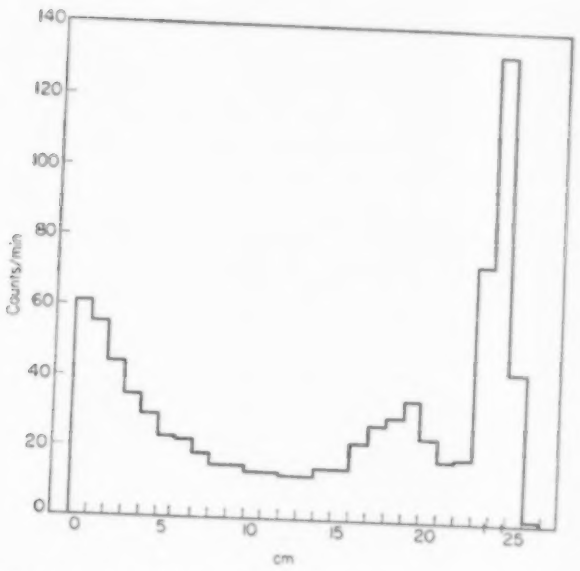

FIG. 5.—Sample irradiated at p.f. 1 for one week. Electrolyte: 0·2 M $NaClO_4$, 0·01 M $HClO_4$.

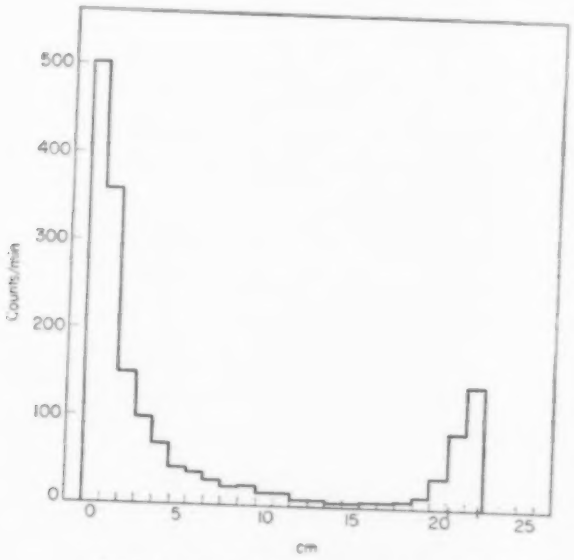

FIG. 6.—As for Fig. 5. Electrolyte 0·2 M $NaClO_4$.

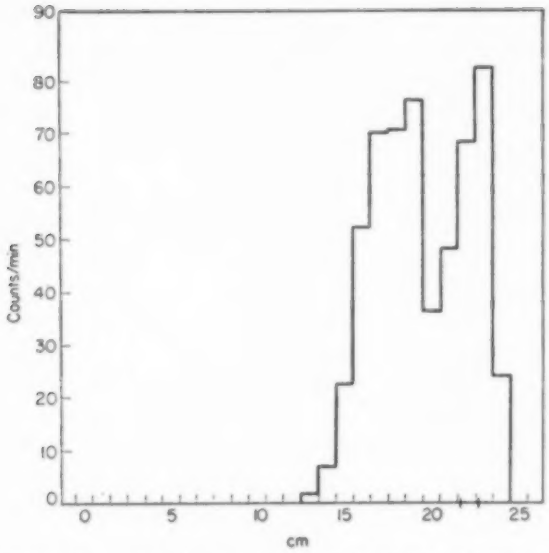

FIG. 7.—Solution of aquochromium bromide labelled with ^{51}Cr. Electrolyte 0·2 M $NaClO_4$, 0·01 M $HClO_4$.

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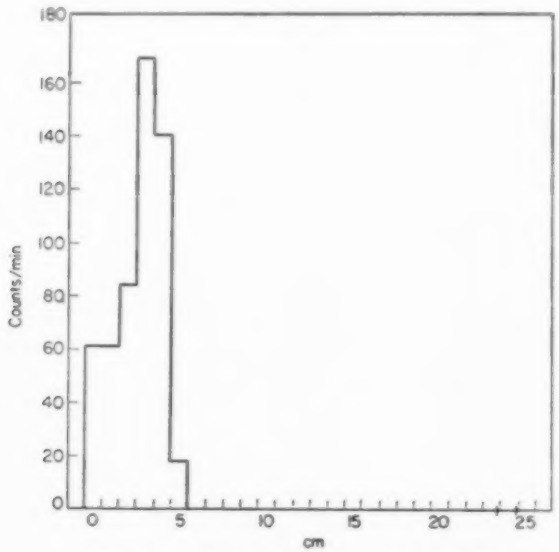

FIG. 8.—As for Fig. 7. Electrolyte 0·2 M $NaClO_4$.

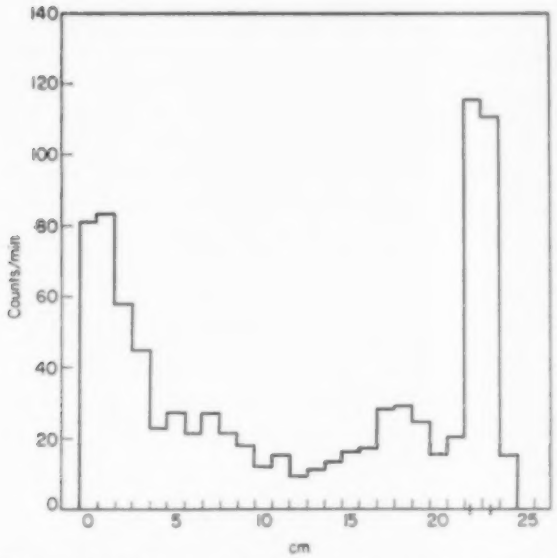

FIG. 9.—Electrophoresis histogram in perchloric solution: conditions as in Fig. 5, but before electrophoresis chromic nitrate was added to the solution and $Cr(OH)_3$ precipitated at pH 8–9. The activity of the solution placed on the strip was 430 counts per minute, that of $Cr(OH)_3$ was 370 counts per minute. The percentages of radioactivity of the single peaks should be multiplied by 430/430+370 in order to be compared with the results of Fig. 5.

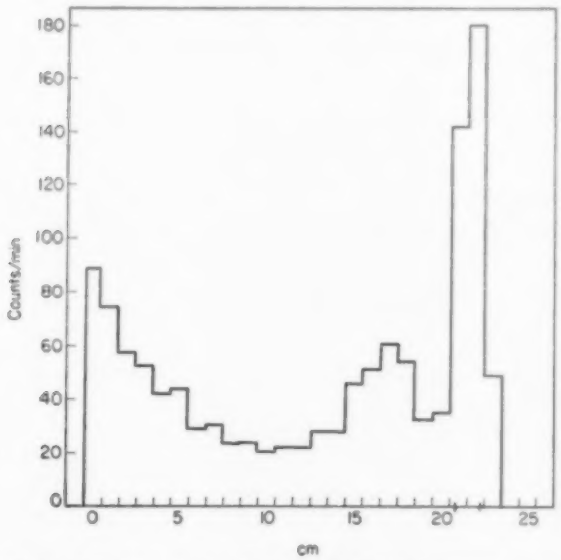

FIG. 10.—Electrophoresis histogram of sample irradiated for one week at p.f.1 (the same as in Fig. 5). Electrolyte: 0·2 M NaCl, 0·01 M HCl. Electrophoresis started immediately after dissolution of crystals.

pH 2 solution, leads to a significant decrease of activity (from 29 to 22 per cent) in the 0–5 cm zone; (compare Fig. 10 with Fig. 11).

The same complications do not allow a clear identification of the radioactive species co-depositing on lead chromate. Nevertheless a tentative explanation may be given. Examination of the electrophoresis patterns shows that the species under consideration in the 0–15 cm zone or the primary parents which produce them, must be formed through γ-annealing, because they appear in larger amounts in cases of samples irradiated at high pile factor, or subjected to γ-irradiation. The values of

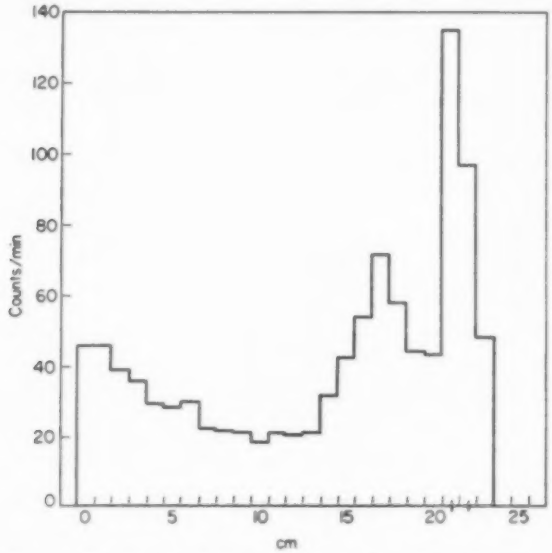

FIG. 11.—Same as Fig. 10 but solution was left standing at room temperature 24 hr before electrophoresis.

the activity in this zone are as follows: Fig. 1, 12 per cent; Fig. 3, 35 per cent; Fig. 5, 30 per cent. This is far the most important increase of activity which can be found in the single zones which have been discussed, and it is comparable with the effects observed in the previous results with lead chromate. We conclude that the species which co-deposit on lead chromate belong to the compounds which are found in this region of the histogram.

A comparison of the above results with those on $CrEn_3(NO_3)_3$ is difficult because of the difference in the irradiation conditions. Considering the figures for Experiment 1) in Table 1, where the conditions of irradiation are likely to be comparable, one observes a good agreement for Cr(VI) but a quite different distribution of activities between Cr(III) and "retained" chromium. Less easily hydrolizable, more stable species (containing less than three ethylenediamine molecules) could be formed in the case of the nitrate due to the change of the anion, consequently leading to an increase of the apparent retention. As to the 6 per cent of activity on the lead chromate found in the nitrate case, one would now be inclined to attribute it to En complexes.

It hardly needs to be emphasised that the results obtained here cannot affect other previous results[2,3] obtained in investigating simple chromic salts. In these cases the

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activity detected on the chromate ions can only be explained by the actual presence of radio-chromium(VI) which is probably formed by oxidation through agents generated in the radiolytic processes.[4]

As to the original purpose of the present work, i.e. the investigation of internal γ-conversion, these results show that in this case there is no evidence in favour of this mechanism. This conclusion is of course subjected to the ordinary limitations which are common to the chemical investigations of these systems; nevertheless we believe that this result is significant, not as a proof of the inapplicability of this mechanism for chromium-51, but because all previous work on chromium compounds, as far as we know, has always led to the detection of chromium oxidation products.

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THE APPLICATION OF THE EFFECTIVE ATOMIC NUMBER RULE TO SOME NEW ORGANO-METALLIC COMPLEXES

DAVID A. BROWN*
Dept. of Chemistry, Queen Mary College, Mile End Road, London

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Abstract—The electronic structures of complexes of the general type $C_nH_nCOFe(CO)_3$ ($n = 2, 4, 6$) have been examined on simple molecular-orbital theory. It is suggested that in the cyclopentadienone and cycloheptatrienone ($n = 4$ and 6) complexes the effective atomic number rule has little significance. In general, it appears that the molecular-orbital point of view provides the most unified picture of the bonding in this series.

THE recent syntheses[1–4] of complexes of the general type $C_nH_nCOFe(CO)_3$ ($n = 4, 6$), that is, cyclopentadienone and cycloheptatrienone (tropone) complexes, raise some interesting problems with regard to the nature of the bonding and, in particular, of the validity of the effective atomic number rule in this series.

The complexes have been prepared both by reaction of acetylenes with iron carbonyls and by direct reaction between the carbonyls and the free ketones at quite moderate temperatures. This latter fact provides good indication that these compounds are true half-sandwich complexes. The presence of the ketonic carbonyl stretching frequency is in further support of this assumption. In addition, a recent communication[5] has suggested that diphenylcyclopropenone is not an intermediate in the carbonylation reaction, and, to the best knowledge of the author, no complexes of this latter compound have yet been prepared. However, in this paper we shall include the hypothetical cyclopropenone complex and show that elementary molecular-orbital theory provides a simple and unified picture of the bonding in this series; it also provides an interesting comment on the effective atomic number rule.

The theoretical methods employed in the subsequent discussion are identical with those of previous papers[6,7] and so they will not be discussed in great detail. The complexes under consideration are:—

cyclopropenone—$Fe(CO)_3$

cyclopentadienone—$Fe(CO)_3$

cycloheptatrienone—$Fe(CO)_3$

* Present address: Dept. of Chemistry, University College, Upper Merrion Street, Dublin.

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[5] C. W. BIRD and J. HUDEC, *Chem. Industr.* 570 (1959)
[6] D. A. BROWN, *J. Inorg. Nucl. Chem.*, **10**, 39, 49 (1959).
[7] D. A. BROWN, *J. Chem. Phys.* **29**, 1086 (1958).

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We assume a typical structure as shown in Fig. 1. It is then assumed that the isolated cyclic ketones are planar and possess C_{2v} symmetry; the π-orbitals are classified under this local symmetry in Table 1. In the complexes, we assume further that the carbonyl groups possess a local trigonal symmetry and, assuming a staggered or eclipsed configuration, it is apparent that the only true symmetry element is the bisecting plane

FIG. 1.—The complex $C_6H_6COFe(CO)_3$.

σ_{yz} (see Fig. 1). Consequently, the orbitals of the constituent parts of the complex may also be classified with respect to this plane, as shown in Table 1. The system C_nH_nCO has been treated on the simple L.C.A.O.M.O. basis using the parameters[8]

$$\alpha_0 = \alpha_c + 2\beta$$
$$\beta_{c0} = \beta_{cc}\sqrt{2}$$

for the cases $n = 2$, 4 and 6.

TABLE 1.—SYMMETRY CLASSIFICATION OF $C_nH_nCOFe(CO)_3$

σ_{yz}	$C_2H_2(CO)$		$C_4H_4(CO)$		C_6H_6CO		Fe	$(CO)_3$
	Orbital Symmetry	Orbital energy (β)	Symmetry	Energy (β)	Symmetry	Energy (β)	Symmetry	Symmetry
	$1a_1$	-3	$1a_1$	$-2{\cdot}95$	$1a_1$	$-2{\cdot}93$	Sp_z	
	$2a_1$	$-1{\cdot}414$	$2a_1$	$-1{\cdot}69$	$2a_1$	$-1{\cdot}82$	d_{z^2}	$a_1(CO)$
+	$3a_1$	$+1$	$3a_1$	$-0{\cdot}194$	$3a_1$	$-0{\cdot}872$	$d_{x^2-y^2}$	
			$4a_1$	$+1{\cdot}85$	$4a_1$	$+0{\cdot}653$	(d_{xy}, p_x)	$e_y(CO)$
					$5a_1$	$+1{\cdot}973$		
	$1b_2$	$+1$	$1b_2$	$-0{\cdot}618$	$1b_2$	$-1{\cdot}247$		
							(d_{xz}, p_y)	$e_x(CO)$
$-$			$2b_2$	$+1{\cdot}618$	$2b_2$	$+0{\cdot}445$		
							d_{yz}	
					$3b_2$	$+1{\cdot}802$		

The nature of the bonding is very similar throughout this series. Let us consider first the antisymmetric group. The orbitals p_x and d_{xz} may be replaced by their sum and difference to give one component overlapping strongly with $e_x(CO)$ and the other with the antisymmetric B_2-orbitals of the aromatic system. Similarly, within the totally-symmetric group (A_1) it is possible to compound the $4s$ and $4p_z$ (and possibly

[8] R. D. BROWN, *J. Chem. Soc.* 2640 (1951).

some $3d_{z^2}$) to give components, one of which overlaps the a_1(CO) orbital and the other which overlaps the A_1-orbitals of the ring system to give μ-type bonding. Finally, one of the d_{yz}/p_y hybrids will overlap with e_y(CO) and the other with the A_1 ring orbitals. As before, we shall neglect any interaction between the $3d_{xy}$ and $3d_{x^2-y^2}$ and the π-orbitals of the aromatic system. The resultant molecular orbitals of the complete complex may then be represented by the symbols

$$\left(na_1, \begin{matrix} 3d/4p \\ 4s/4p \end{matrix}\right) \qquad \text{and} \qquad (mb_2, 3d/4p).$$

The former symbol denotes the bonding orbital (see Appendix) formed by the overlap of the na_1 π-orbital of the ketone with the $3d_{xz}/4p_x$ and $4s/4p_x$ hybrids of the iron atom. Similarly, the latter symbol denotes a bonding interaction between the mb_2 and $3d_{yz}/4p_y$ orbitals. With this notation, it is possible to express the electronic structure of this series of complexes in the form:—

$$(3d_z2)^2\ (3d_{xy})^2\ (3d_{x^2-y^2})^2\ [a_1(\text{CO})4s/4p]^2\ [e(\text{CO})3d/4p]^4$$

$$\left(na_1 \begin{matrix} 3d/4p \\ 4s/4p \end{matrix}\right)^x \qquad (mb_2 3d/4p)^y$$

where $1 \leqslant n \leqslant 4$, $1 \leqslant m \leqslant 2$ and x and y vary between different complexes.

The complexes then differ only in the variation in the number of occupied orbitals of different n and m. As discussed previously,[6] in the case of cyclopentadienone it is necessary to utilize the totally-symmetric orbital ($n = 3$) and the fact that this is relatively low-lying is consistent with the observed stability; it also represents a convenient means of back-donation since the complex orbital is formed from a vacant π-orbital and filled metal orbital.

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The use of this orbital is more reasonable than any of the antibonding orbitals of the type $\left(na_1 \begin{matrix} 4s/4p \\ 3d/4p \end{matrix}\right)^*$. In the case of tropone there are now four filled π-orbitals involved, with a considerable resultant charge-transfer to the metal atom. However, it is found that for this system also there are present vacant and relatively low-lying π-orbitals ($4a_1$ and $2b_2$); again, therefore, a convenient means of back-donation is available. It should be stressed that the presence of this type of orbital seems essential in these latter complexes simply because of the number of electrons involved in the π-component. In the case of cyclopropenone it is not necessary to provide such orbitals. It is possible that some stabilization of the $(1b_2 3d/4p)$ $\left(3a_1 \begin{matrix} 3d/4p \\ 4s/4p \end{matrix}\right)$ orbitals occurs with a resulting back-donation but it is likely to be small in view of the higher energies of the $1b_2$ and $3a_1$ orbitals of cyclopropenone (Table 1). The distribution of electrons in the various orbitals is illustrated in Table 2.

On the basis of simple molecular-orbital theory it is thus possible to represent the bonding in the above series of complexes as a unified whole. It remains to mention briefly the significance of the "Effective Atomic Number Rule" when applied to this series. It is, of course, obvious that this rule is essentially empirical and its interpretation in the sense of a complete filling of the metal $3d$, $4s$ and $4p$ orbitals by electrons which are donated from ligands, π-systems etc. is not in accord with modern valence theory, more especially molecular-orbital theory, since such donation would involve

impossibly large charge transfer.[7] Nevertheless, as an empirical rule it is often useful and, as an example, it serves as a basis for an understanding of the metal carbonyls. In the case of π-complexes formed by the interaction of π-orbitals of the aromatic system with the central metal $3d$, $4s$ and $4p$ orbitals, it is difficult to see how the

TABLE 2.—ELECTRON DISTRIBUTION IN COMPLEXES $C_nH_nCOFe(CO)_3$

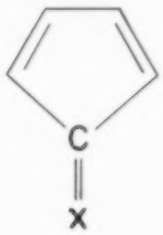
Orbital	C_3H_3CO	Fe	C_4H_4CO	Fe	C_6H_6CO	Fe
$1a_1$ $3d/4p$	2	—	2	—	2	—
$4s/4p$						
$2a_1$ $3d/4p$						
$4s/4p$	2	—	2	—	2	—
$3a_1$ $3d/4p$						
$4s/4p$		(2?)*		2	2	—
$4a_1$ $3d/4p$						
$4s/4p$	—	—	—	—	—	(2?)*
$1b_2$ $3d/4p$		(2?)*	2	—	2	—
$2b_2$ $3d/4p$	—	—	—	—	—	(2?)*

* It is impossible to determine, on this qualitative basis, which orbital will lie at the lower energy.

rule is applicable since, as shown above, one particular metal hybrid orbital may interact with (and stabilize) a number of π-orbitals of the aromatic system, with the same symmetry. This is precisely the difference between the cyclopentadienone and cycloheptatrienone complexes and the presence of electrons in excess of the effective atomic number is common to both. The excess of π-electrons present in these latter complexes is compensated by the presence of vacant low-lying π-orbitals which thereby counteract too large a charge-transfer to the metal atom. This fact does not imply that the effective atomic number rule is still applicable. However, once the π-system provides more than four electrons and, incidentally, thereby exceeds the effective atomic number of the iron atom, it is necessary to invoke the use of the above vacant π-orbitals. The validity of the molecular-orbital approach seems to be substantiated by the fact that the tropone complex possesses the formula, tropone–$Fe(CO)_3$, and not, tropone–$Fe(CO)_2$. It is also note-worthy that thiophene forms the complex thiophene–$Fe(CO)_2$. This is in accord with theory since it has been shown[6] that systems of the type do not possess the relatively low-lying and vacant

orbitals required for the formation of a stable complex C_4H_4X–$Fe(CO)_3$; the complex C_4H_4X–$Fe(CO)_2$ is therefore preferred. However, it has also been shown[6] that systems of the type do possess the required vacant orbital and the existence of

complexes of the type C_4H_4CO–$Fe(CO)_3$ can then be understood. The representation of the bonding in these latter complexes in terms of valence-bond structures such as those shown in Fig. 2 is in accord with the effective atomic number rule. It appears, at



least to the author, that this type of representation is less general than the molecular-orbital approach. It is also a little difficult to see how, even on the valence-bond picture, the effective atomic number rule can be considered valid for the tropone complex.

It is quite possible that less stable complexes containing extra carbonyl ligands may be formed or, equally, that the above series may lose a carbonyl ligand at elevated temperatures. Recent investigations[5] on the mechanism of the carbonylation reaction suggest considerable mobility of the acetylene and carbonyl residues. A similar mobility is revealed in the synthesis[9] of hexaphenylbenzene from diphenylacetylene and tetraphenylcyclopentadienone using a $(i\text{-Bu})_3Al/TiCl_4$ catalyst. The mechanism of this type of reaction and the part undertaken by the above type of complexes presents a fascinating problem to both theorist and experimentalist. The most immediate task is an investigation of the possible radical nature of the reaction.

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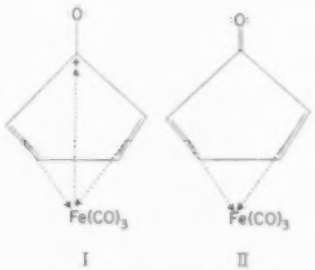


FIG. 2.—Valence-bond representation of C_4H_4CO–$Fe(CO)_3$.

APPENDIX

The interaction of orbitals ψ_2 and ψ_3 is considered, with coulomb terms H_2 and H_3 situated on centre A ,with the orbital ψ_1, Coulomb term H_1, situated on centre B. It is assumed that ψ_2 and ψ_3 are orthogonal. The secular equation, neglecting overlap, takes the form:

$$\begin{vmatrix} H_1 - E & \beta & \gamma \\ \beta & H_2 - E & 0 \\ \gamma & 0 & H_3 - E \end{vmatrix} = 0$$

[9] B. FRANZUS, P. J. CANTERINO and R. A. WICKLIFFE, *J. Amer. Chem. Soc.* **81**, 1514 (1959).

where β and γ represent the resonance integrals between ψ_1 and ψ_3, and ψ_1 and ψ_2 respectively. On expansion this takes the form:

$$f(E) \equiv (H_1 - E)(H_2 - E)(H_3 - E) - \beta^2(H_3 - E) - \gamma^2(H_2 - E) = 0$$

If we further assume $|H_1| > |H_2| > |H_3|$ then by consideration of the variation of $f(E)$ with E we obtain the following result:—

$$f(0) = H_1H_2H_3 - \beta^2H_3 - \gamma^2H_2 < 0$$

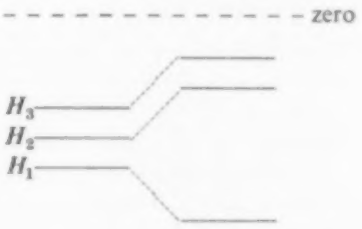
$$f(H_3) = -\gamma^2(H_2 - H_3) > 0$$

$$f(H_2) = -\beta^2(H_3 - H_2) < 0$$

$$f(H_1) = -\beta^2(H_3 - H_1) - \gamma^2(H_2 - H_1) < 0$$

$$f(-\infty) = +\infty > 0$$

The orbital energy diagram takes the following form:



In other words, the interaction of a π-orbital with two orthogonal hybrids of the metal atom leads to the formation of only one bonding orbital.

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THERMODYNAMIC STUDIES OF AMMONIUM HALIDES AND SOME UNIVALENT NITRATES

M. F. C. LADD and W. H. LEE
Chemistry Dept., Battersea College of Technology, London

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Abstract—The lattice energies and free energies of solution of the ammonium halides and of some univalent nitrates and the heat of hydration of the ammonium and nitrate ions, have been calculated. The relationship between the free energy of solution, ΔG_s, and the solubility of each halide is shown to be normal except in the case of ammonium fluoride. The relationship between the free energy of solution ΔG_s, and the solubility of the nitrates is discussed with regard to the very low mean ionic activity coefficients in their saturated solutions.

PART 1. THE LATTICE ENERGIES AND FREE ENERGIES OF SOLUTION OF THE AMMONIUM HALIDES AND THE HEAT OF HYDRATION OF THE AMMONIUM ION

THE lattice energies of the ammonium halides have been calculated by GRIMM[1] and BLEICK[2]; since then, however, considerable revision has been made of compressibility and structural data. It seemed appropriate to recalculate these lattice energies and to determine the free energies of solution of these halides so that the effect of hydrogen bonding in ammonium fluoride might be assessed.

The lattice energies of the chloride, bromide and iodide were computed using an equation previously described[3] and the data listed in Table 1.

TABLE 1.—STRUCTURAL PARAMETERS OF THE AMMONIUM HALIDES

	r_0 (Å)	$10^{12}\,\beta$ (barye^{-1})	$10^{60}\,C$ (erg-cm^6/molecule)	$10^{76}\,D$ (erg-cm^8/molecule)
NH_4Cl	3·356	6·4	700	1000
NH_4Br	3·516	6·5	900	1400
NH_4I	3·79	7·6	1400	2300

The interatomic distances were taken from the latest data in the A.S.T.M. index.[4] The compressibilities were derived by extrapolation of the data of BRIDGMAN[5] and applied to the "cesium chloride" arrangement of these salts; this necessitated the use of the older value of r_0 for ammonium iodide[6] rather than that listed in the A.S.T.M. index which applies to the "sodium chloride" modification of this salt. The values

[1] H. GRIMM, *Handbuch der Physik* **24**, 518 (1927).
[2] W. BLEICK, *J. Chem. Phys.* **2**, 160 (1934).
[3] M. F. C. LADD and W. H. LEE, *Trans. Faraday Soc.* **54**, 34, (1958).
[4] *Index of X-ray Diffraction Data.* A.S.T.M., Pa. (1958).
[5] P. W. BRIDGMAN, *Phys. Rev.* **57**, 237, (1940).
[6] R. W. G. WYCKOFF, *Crystal Structures* Vol. 1. Interscience, New York (1948).

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listed for C and D are considerably lower than those of BLEICK[2]; from a consideration of the additivity of ionic radii it was thought that the C and D values should not differ greatly from those of the rubidium halides,[7] and they have been estimated accordingly.

In Table 2 the lattice energies so calculated are compared with those previously given.

TABLE 2.—LATTICE ENERGIES OF AMMONIUM HALIDES: (kcal/mole)

	Present work	BLEICK	GRIMM	MAY[8]
NH_4F	(187)	(191)	—	—
	—	176	178	—
NH_4Cl	156	162	153	172
NH_4Br	151	154	147	—
NH_4I	142	146	144	—
	(140)	—	—	—

The lattice energy of ammonium fluoride cannot be calculated directly unless the term involving its compressibility (which is not known) is estimated. However, by application of the modified Born–Haber cycle, depicted by equation (1), to the other halides, the heat of formation of the ammonium ion, $\Delta H_f(NH_4^+ \text{ gas})$, was determined and used to evaluate the lattice energy of ammonium fluoride.

$$\Delta H_l = \Delta H_f - \Delta H_f(NH_4^+ \text{ gas}) - E(X) - 1/2D(X_2) \qquad (1)$$

The terms in this equation have been discussed previously.[3] In this way the values shown bracketed in Table 2 were obtained. The values of $\Delta H_f(NH_4^+ \text{ gas})$ were as follows:

NH_4Cl	NH_4Br	NH_4I	
141	142	144	kcal/mole.

Since there is the possibility of error in r_0 for ammonium iodide, the mean of these values was taken to be 142 kcal/g-ion. On this basis the lattice energy of ammonium iodide was found to be 140 kcal/mole, and this value is preferred to that listed first in Table 2. The stable crystalline form of ammonium fluoride has the four-co-ordinated Würtzite structure; this is not predicted from radius ratio considerations and is generally attributed to hydrogen bonding. The extra lattice stability of approximately 10 kcal/mole is undoubtedly due to this effect.

We consider next the calculation of the heat of hydration of the ammonium ion from the equations

$$\Delta H_h(NH_4X) = \Delta H_l(NH_4X) + \Delta H_s(NH_4X) \qquad (2)$$

and

$$\Delta H_h(NH_4^+) = \Delta H_h(NH_4X) - \Delta H_h(X^-) \qquad (3)$$

where ΔH_s is the experimental heat of solution at infinite dilution. Table 3 lists the terms used in this calculation.

[7] M. BORN and K. HUANG, *Dynamical Theory of Crystal Lattices* p. 28. Oxford (1954).
[8] A. MAY, *Phys. Rev.* **52**, 339 (1937).

The value of −78 kcal/g-ion for $\Delta H_h(NH_4^+)$ is in good agreement with that of ALTSCHULLER[11] (−79); this is perhaps fortuitous as his calculation is based on the value $U(NH_4Cl) = -72$ kcal/mole[8] which is probably about 16 kcal too low.

TABLE 3.—HEAT OF HYDRATION OF THE AMMONIUM ION

	$-\Delta H_l$*	ΔH_s	$-\Delta H_h$	$-\Delta H_h(X^-)$[9]	$-\Delta H_h(NH_4^+)$
NH_4F	188	1·2	186·8	108·6	78·2
NH_4Cl	157	3·6	153·4	76·1	77·3
NH_4Br	152	3·9	148·1	69·2	77·9
NH_4I	141	3·2	137·8	60·2	77·6

Mean value: $\Delta H_h(NH_4^+) = -78$ kcal/g-ion.

* $\Delta H_l = U(r_0) - 1$ (kcal/mole).[10]

The free energies of solution of the ammonium halides were calculated:

$$\Delta G_s = \Delta H_s - T\Delta S_s,$$
$$= \Delta H_s - T(\Sigma \bar{S}_i^\circ - S_L) \quad (4)$$

where $\Sigma \bar{S}_i^\circ$ is the sum of the "absolute" partial g-ionic entropies, listed by LATIMER[12] and STEPHENSON.[13] The lattice entropy S_L has been determined experimentally only in the case of ammonium chloride. However, using this value[14] and the empirical equation of LATIMER[15] we have evaluated S_L for the remaining halides. These quantities, and the derived ΔG_s, are listed in Table 4.

TABLE 4.—THE FREE ENERGIES OF SOLUTION OF THE AMMONIUM HALIDES (kcal/mole)

	ΔH_s	$\Sigma \bar{S}_i^\circ$	S_L	$T\Delta S_s$	ΔG_s
NH_4F	1·2	23·9	18·4	1·6	−0·4
NH_4Cl	3·6	39·7	22·6	5·1	−1·5
NH_4Br	3·9	45·9	25·9	6·0	−2·1
NH_4I	3·2	51·5	27·5	7·2	−4·0

The reliability of ΔG_s may be tested, in the case of ammonium chloride, from the equation:

$$\Delta G_s = -RT \ln (a\pm)^{\nu_+ + \nu_-}, \quad = -2RT \ln (a\pm) \quad (5)$$

where $a\pm$ is the mean ionic activity of the saturated solution. Recent experimental values of $a\pm$[16,17] give:

$$\Delta G_s = -1{\cdot}5 \text{ and } -1{\cdot}4 \text{ kcal/mole, respectively.}$$

[8] J. E. B. RANDLES, *Trans. Faraday Soc.* **52**, 1573, (1956).
[10] M. F. C. LADD and W. H. LEE, *J. Inorg. Nucl. Chem.* **11**, 264 (1959).
[11] A. P. ALTSCHULLER, *J. Amer. Chem. Soc.* **77**, 3480 (1955).
[12] W. M. LATIMER, *Oxidation Potentials*. Prentice Hall, New York (1958).
[13] C. C. STEPHENSON, *J. Amer. Chem. Soc.* **66**, 1436 (1944).
[14] W. T. ZIEGLER and C. E. MESSER, *J. Amer. Chem. Soc.* **63**, 2698 (1941).
[15] W. M. LATIMER, *J. Amer. Chem. Soc.* **73**, 1480 (1951).
[16] J. N. PEARCE and G. S. PUMPLIN, *J. Amer. Chem. Soc.* **59**, 1219 (1937).
[17] B. F. WISHAW and R. H. STOKES, *Trans. Faraday Soc.* **49**, 27 (1953).

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Discussion

The decrease in ΔG_s along the series $NH_4Cl \rightarrow NH_4Br \rightarrow NH_4I$ accords well with the known increase in solubility, as shown:

	NH_4Cl	NH_4Br	NH_4I
Molality of sat'd solution.[18]	7·4	8·0	11·5

Ammonium fluoride is, however, anomalous; its molal solubility is 23·2 at saturation,[18] but its ΔG_s suggests that it would be appreciably less soluble than the chloride. In the calculation of ΔG_s from equation (4) we use the terms ΔH_s, ΣS_i°, and S_L. Now, ΔH_s is an experimentally determined quantity, and the additivity of the values of S_i°, indicate that there is no appreciable error in these quantities. The value of S_L is obtained from an empirical equation, as mentioned above, but the results of this approach have been used previously without serious discrepancy.[3] If, then, the value of ΔG_s for ammonium fluoride is accepted, the mean ionic activity coefficient in the saturated solution is approximately 0·06 which, amongst salts of this type, is surprisingly low.

Another salt which has a very small activity coefficient in concentrated solution is silver nitrate: $\gamma\pm = 0{\cdot}09$ in thirteen molal solution.[19] Strong interionic attraction in the concentrated solution would account for these results. Such interaction might be expected, on the one hand from the planarity of the nitrate ion,[19] and the possibility of close approach of the cation to it; and, on the other, from the formation of hydrogen bonds between the ammonium and fluoride ions. It is hoped to confirm this hypothesis by a study of the electrical conductivities of ammonium fluoride solutions.

PART 2. THE LATTICE ENERGIES AND FREE ENERGIES OF SOLUTION OF SOME UNIVALENT NITRATES, AND THE HYDRATION ENTHALPY OF THE NITRATE ION

The role of the lattice energy in determining the solubility of an ionic compound is well known, and often determines such changes in this property as are observed when we compare compounds of an inert-gas type cation with those of a *B*-subgroup cation. For example, silver fluoride is the only soluble silver halide, whilst calcium fluoride is the only insoluble calcium halide; solubility decreases along the series $F \rightarrow Cl \rightarrow Br \rightarrow I$, for the thallium halides, but increases along the same series for the lithium halides. The free energy of solution gives in general a good indication of the molal solubility. Such trends are not observed amongst the metallic nitrates; in particular, those of silver, lithium and calcium are all very soluble. Thallous nitrate is the least soluble of those considered, comparable in solubility with lithium and sodium fluorides.

In order to interpret the free energies of solution of a series of nitrates, it was necessary to calculate their lattice energies. Such calculations have been carried out previously but without the inclusion of terms representing the van der Waals attractive forces.[20,21,22] Other values have been obtained from a consideration of

[18] A. SEIDEL, *Solubility of Inorganic Compounds*. D. Van Nostrand, New York (1940 and 1952).
[19] R. A. ROBINSON and R. H. STOKES, *Trans. Faraday Soc.* **45**, 612 (1949).
[20] J. TOPPING and S. CHAPMAN, *Proc. Roy. Soc.* A **113**, 658 (1927).
[21] K. HOJENDAHL, *Kgl. Danske Videnskal Selskab, Mat-phys. Medd.* **16**, 133 (1938).
[22] T. C. WADDINGTON. *Advances in Inorganic and Radiochemistry* Vol. I, p. 201. Academic Press, New York (1959).

lyotropic numbers.[22,23] The usual Born–Haber cyclic process for the calculation of lattice energy requires the term $\Delta H_f(NO_3^-$ gas), i.e. the heat of formation of the gaseous nitrate ion; in order to obtain this quantity, lattice energies were calculated by the method indicated in the first part of this paper, where this was applicable. The nitrates of cesium, ammonium and rubidium, in their cesium chloride modification, are amenable to this calculation; the relevant structural parameters are listed in Table 5.

TABLE 5.—STRUCTURAL PARAMETERS OF THE CsCl MODIFICATIONS OF NH_4NO_3, $RbNO_3$ AND $CsNO_3$

	r_0 (Å)	$10^{12}\beta$ (barye^{-1})	10^{60} C (erg-cm^6/molecule)	10^{78} D (erg-cm^8/molecule)
NH_4NO_3	3·81	6·7	800	1200
$RbNO_3$	3·79	4·6	700	1000
$CsNO_3$	3·89	4·6	1600	2800

The C and D terms have been estimated from a consideration of the polarizabilities of the ions. From the interionic distances listed by WYCKOFF[6] the nitrates appear comparable in size with the corresponding iodides; however, the polarizability of the nitrate ion is much smaller than that of the iodide ion.[24]

The compressibilities, β, have been obtained by extrapolation of the data of BRIDGMAN relevant to the appropriate modifications.[25] The lattice energies so calculated were:

	NH_4NO_3	$RbNO_3$	$CsNO_3$	
$U(r_0)$	143	147	144	kcal/mole

Application of the Born–Haber cycle, in the form:[3]

$$\Delta H_l = \Delta H_f - I_M - S_M - \Delta H_f(NO_3^-\text{ gas}) \qquad (6)$$

leads to the following values for the last term in equation 6:

	NH_4NO_3	$RbNO_3$	$CsNO_3$	
$\Delta H_f(NO_3^-$ gas)	−85	−86	−82	kcal/g-ion

The average value is −84 kcal/mole, and this is used, in equation (6) as applied to the remaining nitrates, to calculate their lattice enthalpies; the results were:

	$LiNO_3$	$NaNO_3$	KNO_3	$AgNO_3$	$TlNO_3$	
ΔH_l	193	173	157	190	159	kcal/mole

The series follows closely that of the corresponding halides, and again silver is intermediate in lattice enthalpy between lithium and sodium.

We next calculate the heat of hydration of the gaseous nitrate ion at infinite

[23] D. F. C. MORRIS, *J. Inorg. Nucl. Chem.* **6**, 295 (1958).
[24] C. J. F. BÖTTCHER, *Rec. Trav. Chim.* **65**, 19 (1946).
[25] P. W. BRIDGMAN, *Proc. Amer. Acad. Arts Sci.* **76**, 1 (1945).

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dilution, $\Delta H_h(NO_3^-$ gas). By analogy with equations (2) and (3), in the first part of this paper, the values listed in the last column of Table 6 were calculated from:

$$\Delta H_h(NO_3^-\text{ gas}) = \Delta H_l(MNO_3) + \Delta H_s(MNO_3) - \Delta H_h(M^+)$$

TABLE 6.—THE HYDRATION ENTHALPY OF THE GASEOUS NITRATE ION

	$-\Delta H_l$*	ΔH_s	$-\Delta H_h(MNO_3)$	$-\Delta H_h(M^+)$†	$-\Delta H_h(NO_3^-$ gas)
$LiNO_3$	194	−0·7	194·7	131·6	63·1
$NaNO_3$	173	4·9	168·1	106·0	62·1
KNO_3	157	8·4	148·6	85·9	62·2
$RbNO_3$	148	8·7	139·3	80·3	59·0
$CsNO_3$	144	9·5	134·5	72·3	62·2
NH_4NO_3	144	6·2	137·8	78	59·8
$AgNO_3$	190	5·4	184·6	123·1	61·5
$TlNO_3$	159	10·0	149	86·2	62·8

Mean $\Delta H_h(NO_3^-$ gas) = -61 ± 2 kcal/g-ion

* The lattice energy $U(r_0)$ is related to the lattice enthalpy ΔH_l by the relationship: $\Delta H_l = U(r_0) - 1$.[10a]
† The data for $\Delta H_h(M^+)$ are from RANDLES[9] except in the cases $M = NH_4$, Ag and Tl, which have been calculated by the authors (e.g. Table 3 of Part I of this paper).

In Table 7 the free energies of solution of these nitrates are calculated from heats and entropies of solution. The activities ($a\pm$) of the saturated solutions are derived, and, in conjunction with the mean ion activity coefficients ($\gamma\pm$) at saturation,* the molarities (m) are computed.

TABLE 7.—FREE ENERGIES OF SOLUTION OF NITRATES AND SATURATION MEAN-ION ACTIVITIES AND MOLALITIES

	ΔH_s	ΣS_i°	S_L	$T\Delta S_s$	ΔG_s	$a\pm$	$\gamma\pm$	m
$LiNO_3$	−0·7	38·4	25·2	3·9	−4·6	49·2	3·78	13·0
$NaNO_3$	4·9	49·4	27·8	6·4	−1·5	3·57	·331	10·8
KNO_3	8·4	59·5	31·8	8·3	0·1	0·92	·263	3·5
$RbNO_3$	8·7	64·7	33·6	9·3	−0·6	1·66	·369	4·5
$CsNO_3$	9·5	66·8	35·3	9·4	0·1	0·92	·613	1·50
NH_4NO_3	6·2	62·0	36·1	7·7	−1·5	3·55	·137	25·9
$AgNO_3$	5·4	52·7	33·7	5·7	−0·3	1·29	·096	13·5
$TlNO_3$	10·0	65·4	37·1	8·4	1·6	0·26	·556	0·45

Discussion

The free energy of solution is seen to be appreciably positive only for thallium nitrate, making this the least soluble of the nitrates considered. Apart from this compound, the relationship between ΔG_s and solubility is not as straightforward as

* Extrapolated from the data of CONWAY.[38]

[38] B. E. CONWAY, *Electrochemical Data*. Elsevier, New York (1952).

in the case of the alkali halides.[3] ΔG_s has the value $-1{\cdot}5$ kcal/mole for both $NaNO_3$ and NH_4NO_3; their saturation molalities are, however, 11·2 and 27·3, respectively. Conversely, lithium and silver nitrates have very similar molalities at saturation; yet the ratio of their ΔG_s's is about fifteen.

Since the effective radius of the nitrate ion in the crystal lattice is comparable with that of the iodide ion, it is interesting to compare salts of these two anions with the univalent cations considered. For both iodides and nitrates, ΔH_s increases along the series Li–Na–NH_4–K–Rb–Cs: ΔS_s also increases, though more slowly, along this series; hence ΔG_s ($=\Delta H_s - T\Delta S_s$) *increases* along the series, and solubility decreases. In the case of silver and thallium nitrates, however, ΔH_s is much smaller than for the corresponding iodides, reflecting mainly a relative *increase* in lattice energy. In general, the lattice enthalpy ΔH_l of a nitrate is lower than that of the iodide, but this difference is reversed for silver and thallium compounds:

$\Delta H_l(MI) - \Delta H_l(MNO_3)$, M =	Li	Na	K	NH_4	Rb	Cs	Ag	Tl
kcal/mole	20	10	6	4	3	7	−20	−6

and this in turn arises from the reduced homopolar component of lattice energy in $AgNO_3$ and $TlNO_3$, as compared with Ag(I) and Tl(I); their much greater solubilities are thus explained.

The molal solubilities depend, of course, upon the mean ion activity coefficients, as well as upon ΔG_s; equating ΔG_s to $-RT \ln (a\pm)^2$, we obtain the saturation activities listed in Table 7. Now apart, perhaps, from $LiNO_3$, all the nitrates show abnormally low activity coefficients in solution, so that much more of the salt has to dissolve, to produce a comparable reduction in free energy, than would be the case for the corresponding iodide. The (negative) value of ΔG_s for lithium nitrate corresponds to a saturation activity of 49·2, which is attained in 15-molal solution, in which $\gamma\pm = 3{\cdot}2$. The saturation activity of silver nitrate is only 1·29; yet this is attained in 14-molal solution, for $\gamma\pm$ is here 0·09.

The high molal solubilities of most nitrates are largely due, then, to very low activity coefficients in concentrated solutions, rather than to large negative ΔG_s's. The low activity coefficients of nitrates have been observed previously in dilute solutions, where the effects are smaller;[27,28] they are ascribed to ion-pair formation, which is favoured by the possibility of close approach of cations to the "flat" nitrate ion, and the resulting small effective Bjerrum distance.[29]

[27] C. W. DAVIES, *Trans. Faraday Soc.* **23**, 351 (1927).
[28] R. A. ROBINSON and C. W. DAVIES, *J. Chem. Soc.* 574 (1937).
[29] N. BJERRUM, *Selected Papers*. Copenhagen (1949).

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J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 225 to 230. Pergamon Press Ltd. Printed in Northern Ireland

HEATS OF COMBUSTION AND FORMATION OF LOWER MEMBERS OF METHOXY END-BLOCKED DIMETHYLPOLYSILOXANES

T. TANAKA
Department of Applied Chemistry, Faculty of Engineering
Osaka University, Osaka, Japan

(*Received* 25 *August* 1959)

Abstract—The heats of combustion of dimethyldimethoxysilane (I), 1,3-dimethoxytetramethyldisiloxane (II) and 1,5-dimethoxyhexamethyltrisiloxane (III) have been measured at 20°C and constant volume, and from the results the corresponding heats of combustion and formation in the isobaric process have been calculated to be (I) 832, 171, (II) 1295, 301 and (III) 1771, 425 kcal/mole, respectively. Further the sum of bond energy values on the structural unit of C_2SiO_2,* $-E\left[\begin{array}{c} C \\ | \\ O-Si-O \\ | \\ C \end{array}\right]$, in these compounds has been derived from the heats of formation, and discussed by comparing with that expected from additive law of bond energy.

THE heats of formation of lower members of polydimethylsiloxanes have already been obtained from the combustion experiments of THOMPSON[1], and bond energy terms of the Si—O and Si—C bonds were derived to be 117 and 64 kcal/mole, respectively, on the basis of values of 171·7 and 88·04 kcal/g atom for heats of atomization of carbon and silicon, respectively. Of these bond energies, the former seems to be too high and the latter somewhat low by comparing with the values calculated from heats of formation of silica and carborundum. In fact, the Si—O bond energy term is already derived to be 102 kcal/mole from the heats of formation of methoxy-silane and -siloxanes, $CH_3O\left[\begin{array}{c} OCH_3 \\ | \\ Si \cdot O \\ | \\ OCH_3 \end{array}\right]_n \cdot CH_3$ ($n = 1$–3), and this value was found to be somewhat lower than that for amorphous silica.[2] In the preceding paper,[3] however, it has been observed that the bond energy value of the Si—O bond in methyl- and ethyl-methoxypolysiloxanes, $CH_3O\left[\begin{array}{c} R \\ | \\ Si \cdot O \\ | \\ OCH_3 \end{array}\right]_n \cdot CH_3$ ($R = CH_3$ or C_2H_5, $n = 1$–3), having the structural unit of $CSiO_3$, would be less than that in methoxy-silane and -siloxanes, the structural unit being SiO_4, and this fact has been considered to be due to a decrease

* In this paper, the silicon tetrahedron indicated by C_nSiO_{4-n} ($n = 0$–4), in which C—H and C—O bonds are excepted, has expediently been considered as the structural unit.

[1] R. THOMPSON, *J. Chem. Soc.* 1908 (1953).
[2] T. TANAKA and T. WATASE, *Bull. Chem. Soc. Japan* **28**, 258 (1955).
[3] T. TANAKA, *Bull. Chem. Soc. Japan* **32**, 1258 (1959).

in the number of resonance structures between Si—O bonds in the $CSiO_3$ unit, compared with in the SiO_4 unit.

In the present work, heats of combustion of the members represented by K_n have been measured, and the corresponding heats of combustion and formation in the isobaric process and the sum of bond energies of bonds containing the silicon atom have been calculated, and these thermal data have been discussed.

$$K_n;\quad CH_3O\left[\begin{array}{c}CH_3\\|\\Si{\cdot}O\\|\\CH_3\end{array}\right]_n{\cdot}CH_3,\quad n=1\text{–}3.$$

EXPERIMENTAL

Materials. The preparations and the physical constants of members of K_n used in this work have already been reported.[4]

Calorimetry. The apparatus used in this experiment is described elsewhere.[2,5] Calibration experiment of the calorimeter have been made at 20°C using benzoic acid (39f) supplied by the National Bureau of Standards, Washington, and the energy equivalent of the calorimeter has been determined to be 2465 cal/degree (relative mean deviation ±0·1 per cent).

In the combustion experiment of the organosilicon compounds, silica produced during the early stage of combustion floats over the surface of sample, so there is deficiency of oxygen beneath it, and incompletely burned residue remains on the combustion vessel. Techniques which lead complete combustion of organosilicon compounds have been reported.[1,5,6] It seems, however, that satisfactory combustion is not always obtained even when these techniques were employed. In this experiment, troublesome techniques like these have not been employed; liquid samples have been weighed in a gelatine capsule, with a known heat of combustion, and the capsule has been supported on a platinum combustion vessel by a platinum ignition wire, passing through two small holes in the top of the capsule. After burning of the sample by electrical ignition, carbon monoxide could not be identified by WINKLER's reagent[7] in the gaseous phase of the bombs contents, and a bulky product, consisting of silica and incomplete combustion product, has been found in the combustion vessel. The incomplete combustion product has been found to contain amorphous carbon and, sometimes, a trace of carborundum.

These liquid samples have comparatively low boiling points, and small amounts evaporate through the small holes in the top of the capsule after the weighing of the sample and before ignition (about 1/2 hr). It has been assumed that the amount of each compound that evaporated under 30 atm pressure (initial pressure of bomb reaction) was equal to that under an atmospheric pressure. The amount of evaporation through the small holes at an atmospheric pressure and 18°C (initial temperature of bomb reaction) has been determined to be 1·8, 0·8 and 0·2 mg/hr for the K_1, K_2 and K_3, respectively. In this way, net amounts of each compound subjected to the combustion have been obtained by subtracting the amount of evaporation from the amount of weighed sample. The incomplete combustion products have been determined in quantity by the procedure described elsewhere,[6] and thermal corrections for them have been calculated using values of 7·84 cal/mg (= 32·8 J/mg[9]) and 6·86 cal/mg for the heats of combustion of carbon and carborundum, respectively. The latter value, being that at standard constant volume, has been calculated from the value of −26·7 kcal/mole for the heat of formation of carborundum.[10] The completeness of combustion of K_n has been found to be 98·5–99·7 per cent by the analysis of the incomplete combustion product.

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[4] T. TANAKA and R. ŌKAWARA, *Bull. Chem. Soc. Japan* **28**, 364 (1955).
[5] T. TANAKA, U. TAKAHASHI, R. ŌKAWARA and T. WATASE, *Bull. Chem. Soc. Japan* **28**, 15 (1955).
[6] S. TANNENBAUM, S. KAYE and G. F. LEWENZ, *J. Amer. Chem. Soc.* **75**, 3753 (1953).
[7] L. W. WINKLER, *Z. Anal. Chem.* **102**, 99 (1935).
[8] T. TANAKA, *Technol. Repts. Osaka Univ.* **8**, 437 (1958).
[9] F. D. ROSSINI, *Experimental Thermochemistry* p. 46. Interscience, New York (1956).
[10] F. D. ROSSINI, D. D. WAGMAN, W. E. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamic Properties*. N. B. S., Washington (1952).

RESULTS AND DISCUSSION

Five to seven combustion experiments have been carried out with each liquid sample, and the results are shown in Table 1. Relative mean deviation in each run is somewhat high compared with modern precision measurement. It is, however, of sufficient precision for the purpose of calculating bond energies in view of the other uncertainties involved.

TABLE 1.—EXPERIMENTAL RESULT FOR K_n(cal/g)

Compound	Heat of combustion	Mean
K_1	6834 6839 6827 6843 6834 — —	6827
K_2	6643 6632 6659 6650 6636 6670 6646	6641
K_3	6580 6577 6591 6582 6575 6588 —	6582

Table 2 is a summary of the thermal data of K_n calculated from the combustion results. Notations in Table 2 are as follow: ΔU_R, the heat of combustion at standard constant volume process where the reactants are at 1 atm pressure; ΔH_c, the heat of combustion in the isobaric process at 1 atm pressure; ΔH_f, the heats of formation of the liquid compounds under consideration from standard elements (gaseous oxygen

TABLE 2.—HEATS OF COMBUSTION AND FORMATION OF K_n(kcal/mole)

Compound	Mol. wt.	$-\Delta U_c$	$-\Delta H_c$	$-\Delta H_f$	$-\Sigma E$
K_1	120·226	822	823	171	1683
K_2	194·384	1292	1295	301	2617
K_3	268·542	1767	1771	425	3546

and hydrogen, graphitic carbon and metallic silicon); ΣE, the heats of formation of the gaseous compounds from mono-atomic gases. These energy values have been calculated by the method described in the previous paper.[2] In the calculation of ΣE, heats of vaporization (H_v) have been estimated to be 7·5, 8·6 and 9·5 kcal/mole from the Trouton's rule for K_1, K_2 and K_3, respectively, and heats of atomization for constituent elements of these compounds have been adopted to be 59·2,[10] 52·1,[10] 171·7[10] and 89·9[11] kcal/g atom for oxygen, hydrogen, carbon and silicon, respectively. Although the latter two values of heats of atomization seem to be considerably questionable, this adaptation has been made in order to discuss bond energies from the same standpoint as the previous papers.[2,3] In this way, the ΣE is obtained from ΔH_f of K_n, having formulae of $Si_aC_bH_cO_d$, by the following expression:

$$\Sigma E = \Delta H_f - 89{\cdot}9a - 171{\cdot}7b - 52{\cdot}1c - 59{\cdot}2d - H_v \qquad (1)$$

[11] E. C. BAUGHAN, *Quart. Rev.* 7, 103 (1953).

Bond energy term. According to the additive law of bond energy, the value of ΣE may also be given by the expression

$$\Sigma E = pE_{\text{Si—O}} + qE_{\text{Si—C}} + rE_{\text{C—O}} + sE_{\text{C—H}} \qquad (2)$$

where E represents the bond energy term of the bond corresponding to each suffix, and the factors p, q, r and s are the number of bonds in the compound under consideration. Reasonable values of C—H and C—O bond energies can easily be estimated from heats of formation of normal paraffins and ether, and if it is assumed that each value does not vary from molecule to molecule, the sum of bond energy values of bonds containing the silicon atom may be estimated by Formula (2). In this manner, the sum of bond energies in the structural unit of C_2SiO_2, $-E\left[\begin{array}{c} C \\ | \\ O—Si—O \\ | \\ C \end{array}\right]$, have been derived from ΣE, using 98·8 and 83·2 kcal/mole for C—H and C—O bond energies, respectively, and is shown in Table 3 together with values[3] of $-E\left[\begin{array}{c} C \\ | \\ O—Si—O \\ | \\ O \end{array}\right]$, which is the sum of the bond energies for the structural unit of $CSiO_3$ in methyl- and ethyl-methoxypolysiloxanes (L_n and L'_n, respectively). The C—H bond energy* adopted here has been calculated from the heats of formation of lower members (from ethane to hexane) in normal paraffins,[12] other than methane, and the C—O bond energy from the heat of formation of dimethylether[10] using the above C—H bond energy.

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Two kinds of Si—O bond are contained in K_n; in the Si—O—CH_3 linkage and in the Si—O—Si linkage, but no energy difference of them was observed in the previous paper on methoxy-silane and -polysiloxanes.[2] Accordingly, the bond in these linkages will not be distinguished from each other in the following discussion. In Table 3, the $-E\left[\begin{array}{c} C \\ | \\ O—Si—O \\ | \\ C \end{array}\right]$ increases in value with polymer size of K_n, and its energy difference between K_2 and K_3 is not so large as that between K_1 and K_2. This tendency is similar to that of L_n, and will suggest that these sums of bond energies are close to constant values as the polymer size increases. This tendency for bond energy will always be found in lower members of a homologous series; for example, in calculations of C—C bond energy from the heats of formation of normal paraffins, under assumption that the C—H bond energy is constant for each member.

It will be assumed here for the convenience of discussion that the Si—O bond energy in tetramethoxysilane and the Si—C bond energy in tetramethylsilane are

* Calculated to be 83·2 kcal/mole for C—C bond energy together with this.

[12] F. D. ROSSINI, K. S. PITZER, R. L. ARNETT, R. M. BRAUN and G. C. PIMENTEL, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds.* Carnegie Institute of Technology, Pittsburgh (1953).

normal values for their bond energies. In this case, the normal Si—O and Si—C bond energies should be calculated to be 103* and 71 kcal/mole from the heats of formation of $Si(OCH_3)_4$[2] and $Si(CH_3)_4$[6], using the heats of atomization and the bond energy terms used in this paper. Both of these values are one kcal lower than those† for amorphous silica and carborundum, respectively, and seem to be reasonable for their

TABLE 3.—THE SUM OF BOND ENERGIES IN STRUCTURAL UNITS OF C_2SiO_2 AND $CSiO_2$ (kcal/mole)

Polymer size	$-E\left[\begin{array}{c}C\\\vert\\O-Si-O\\\vert\\C\end{array}\right]$ (K_n)	$-E\left[\begin{array}{c}C\\\vert\\O-Si-O\\\vert\\O\end{array}\right]$ (L_n)	$(L)'_n$
1	329	364	—
2	335	368	368
3	336	370	—
From the additive law	348	380	380

normal bond energies. If this assumption is accepted, the calculated value for $-E\left[\begin{array}{c}C\\\vert\\-O-Si-O\\\vert\\C\end{array}\right]$ result in 348 kcal/mole, and the observed values for K_2 and K_3, and particularly for K_1, are considerably lower than it. Similar lowering of bond energy has been found in L_n and L'_n.[3]

The electronegativity of silicon is fairly small[13] and the covalent radius of it is considerably larger than that of the carbon atom, and it is well known that the silicon atom is, frequently, able to form a partial double bond with atoms having a lone-pair of electrons or electron donating power, by use of its vacant *d*-orbital.[14] Considering these characters, the bonding orbitals of the silicon atom seems to be apt to undergo any distortion by the effect of neighbouring groups, and the lowering of bond energy described above will mainly be attributed to the Si—O and the Si—C bonds, rather than to all of the bonds in the molecule under consideration.

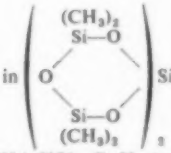
* Hereafter, this will be adopted as the more proper value rather than 102 kcal/mole in the previous paper,[2] in which the values of 98·9 and 84·1 kcal/mole were used for the C—H and the C—O bond energies, respectively.

† See Ref. 2 for the Si—O bond energy in amorphous silica. The Si—C bond energy in carborundum has been calculated to be 72 kcal/mole from the heat of formation of carborundum.[6]

[13] H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1955); A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 264, 269 (1958).

[14] For example, F. G. A. STONE and D. SEYFERTH, *J. Inorg. Nucl. Chem.* **1**, 112 (1955).

It is well known that the observed atomic distance[15] of the Si—O bond is abnormally shorter than that (1·91 Å) expected from the sum of the covalent radii, and this shortening has been considered to be due to contribution of d_π—p_π bond character.[16] The π-bond character of each Si—O bond in the C_2SiO_2 unit will be undoubtedly less than that in the $CSiO_3$ and SiO_4 units, and it may decrease in quantity with decreasing of the number of oxygen attached to silicon, considering the resonance hybrid forms between Si—O bonds. Accordingly, the bond energy value of the Si—O bond will be supposed to become lower as the number of oxygen atom attached to silicon decreases; $-E_{Si-O}$ in the SiO_4 unit $> -E_{Si-O}$ in the $CSiO_3$ unit $> -E_{Si-O}$ in the C_2SiO_2 unit. This supposition on Si—O bond energy will correspond to shortening of the silicon-halogen bond distance with decreasing number of halogen atom attached to silicon,[15c] and may be appropriate considering that the lowering of bond energy in each member of K_n, especially K_1, is larger than that in the corresponding member of L_n.

[15] For examples (a) 1·64 ± 0·03 Å in  Si, W. L. ROTH and D. HARKER, *Acta Cryst.* **1**, 34 (1948); (b) 1·66 ± 0·04 Å in $[(CH_3)_2SiO]_3$, E. H. AGGARWAL and S. H. BAUER, *J. Chem. Phys.* **18**, 42 (1950); (c) 1·64 ± 0·03 Å in $Si(OCH_3)_4$ and 1·63 ± 0·05 Å in $((CH_3)_3Si)_2O$, M. YOKOI, *Bull. Chem. Soc. Japan.* **30**, 106 (1957).

[16] L. PAULING, *J. Phys. Chem.* **56**, 361 (1952).

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A NEW PHOSPHORUS SULPHIDE PHASE

G. A. RODLEY and C. J. WILKINS
Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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Abstract—A new phosphorus sulphide phase may be obtained from melts of composition within the range P_4S_5–$P_4S_{6.5}$. The X-ray powder pattern expands as the sulphur content of the melt falls. It is deduced that the phase is of variable composition. When red phosphorus is used as a reactant, addition of iodine is necessary to give a substantial yield of the new phase. Otherwise P_4S_7 is the chief product. The new sulphide is also formed from the reaction between hydrogen sulphide and phosphorus trichloride. It melts incongruently at 250° with separation of P_4S_7 and also decomposes below 200°. However, it persists for a few months at ordinary temperature. Extraction with carbon disulphide causes decomposition to P_4S_7 and P_4S_3.

THE question as to the existence of a phosphorus sulphide P_4S_6* has been much investigated. Earlier claims for such a compound[1] were discounted by MAI,[2] and by HELFF,[3] who concluded from vacuum sublimation studies that the preparations contained P_4S_7 and P_4S_3. Furthermore, BOULOUCH[4] reported that melts of composition P_4S_6 could be resolved by a combination of fractional crystallization and solvent extraction into P_4S_3 and "P_2S_5", but added that the latter "is not necessarily a definite compound". Contrary to GIRAN,[5] STOCK found a maximum in the melting point curve for the phosphorus-sulphur system at the composition P_4S_7 and considered this to be the only compound of composition intermediate between P_4S_3 and P_4S_{10}.[6] However, there is difficulty in making melting point observations as the proportion of sulphur is reduced below the composition P_4S_7 owing to the increasingly high viscosity of the melt, its deep colour, and its tendency to supercool. Consequently the individual melting point determinations showed considerable scatter and the possible existence of one or more compounds melting incongruently cannot be excluded.

A sulphide P_4S_5 had been reported by BOULOUCH[7] a little before STOCK's work. Doubt concerning its individuality seems to have existed until 1935 when TREADWELL and BEELI[8] confirmed its identity and reported its appearance, along with P_4S_7, as a product from the solvent extraction of a sulphide sample of total composition P_4S_6. Very recent evidence[9] from X-ray powder photography and solvent extraction suggests that the product of empirical composition P_4S_6 from the reaction between phosphorus trichloride and hydrogen sulphide is also a mixture of P_4S_5 and P_4S_7.

* The arbitrary formulation P_4S_6 is used to facilitate comparison with the adjacent sulphides, P_4S_5 and P_4S_7.

[1] For earlier reference see J. W. MELLOR, *Comprehensive Treatise in Inorganic and Theoretical Chemistry* Vol. VIII, pp. 1047–1054. Longmans, Green, London (1928).
[2] J. MAI, *Liebigs Ann.* **265**, 192 (1891).
[3] A. HELFF, *Z. Phys. Chem.* **12**, 196 (1893).
[4] R. BOULOUCH, *C.R. Acad. Sci., Paris* **143**, 41 (1906).
[5] H. GIRAN, *C.R. Acad. Sci., Paris* **142**, 398 (1906).
[6] A. STOCK, *Ber. Dtsch. Chem. Ges.* **42**, 2062 (1909).
[7] R. BOULOUCH, *C.R. Acad. Sci., Paris* **138**, 363 (1904).
[8] W. P. TREADWELL and C. BEELI, *Helv. Chim. Acta* **18**, 1161 (1935).
[9] A. R. PITOCHELLI and L. F. AUDRIETH, *J. Amer. Chem. Soc.* **81**, 4458 (1959).

In seeking confirmation, by X-ray powder photography, of TREADWELL and BEELI's conclusion that P_4S_7 and P_4S_5 are the constituents of sulphide samples of overall composition P_4S_6 obtained by firing red phosphorus and sulphur, we found the situation more complicated than had hitherto been suspected. The samples contained principally P_4S_7, with smaller proportions of P_4S_3 and of a new sulphide phase, and about 0·2 per cent of a black residue insoluble in carbon disulphide. On the other hand the new phase alone was formed upon solidification of melts of the same total composition P_4S_6 made up from P_4S_3 and either sulphur or P_4S_7. Addition of a trace of iodine enabled formation of the phase from red phosphorus and sulphur or P_4S_7.

True to the finding of BOULOUCH[4] (whose reactants were P_4S_3 and sulphur) crystals, large enough for removal by hand, separated from the melts during slow cooling. Both the tabular lemon yellow crystals and the solid from subsequent slow crystallization of the residual viscous liquid gave the X-ray powder pattern of the new phase. Yet the differing melting ranges of the first crystals (250–295°, after sintering at 235°) and the residue (210–250° approximately, with sintering at 170°) are indicative of segregation.

It was found that the composition of melts must be close to P_4S_6 to promote the growth of relatively large crystals, but the same X-ray powder pattern is produced, without modification by lines from other sulphides, from samples whose compositions extend from $P_4S_{6·75}$ to $P_4S_{5·5}$. A new line, for which $d = 5·36$, develops as the sulphur content falls. Most samples of total composition P_4S_5 gave the unmodified pattern but were not completely crystalline; others contained P_4S_3 and P_4S_7 also. Samples of composition $P_4S_{6·85}$ and $P_4S_{6·9}$ produced the new phase in admixture with the heptasulphide. When the sulphur content was increased to P_4S_7 it was no longer possible to obtain the new phase, even when crystallization occurred within the temperature range of its stability (p. 233).

The composition of the new phase

Attempts to purify such crystals by re-crystallization from solvents or by vacuum sublimation caused decomposition. Analysis of two different preparations of the better grown crystals (from melts of composition P_4S_6) given no treatment beyond careful surface cleaning gave: (i) P, 38·1; S, 60·9%; and the ratio P : S = 4 : 6·18. (ii) P, 36·8; S, 61·8%; P : S = 4 : 6·49 (P_4S_6 requires P, 39·24; S, 60·76%). The alternative method (p. 236) of weighing the P_4S_3 removed by vacuum sublimation following thermal decomposition gave the composition of another sample as $P_4S_{6·5}$. While the exact composition of a sample of the crystalline material might be influenced slightly by traces of included impurity there is no doubt that the sulphur content of the crystals is higher than that of the "P_4S_6" melt from which they separate.

The content of the unit cell of the new crystalline phase was determined from X-ray rotation and Weissenberg photographs. The latter showed the cell to be orthorhombic, and systematic absences of reflexions defined the space group as Pbcn.[10] The cell lengths were $11·4_{(+)}$, $11·4_{(-)}$ and 8·2 Å, and the density 2·09. With four molecules per unit cell the statistical composition would be $P_4S_{6·6}$. No simple formulation of the sulphide (e.g. P_3S_5) satisfies the X-ray data.

[10] N. F. M. HENRY and K. LONSDALE (Editors), *International Tables for X-ray Crystallography* Vol. 1, p. 149. Kynoch Press, Birmingham (1952).

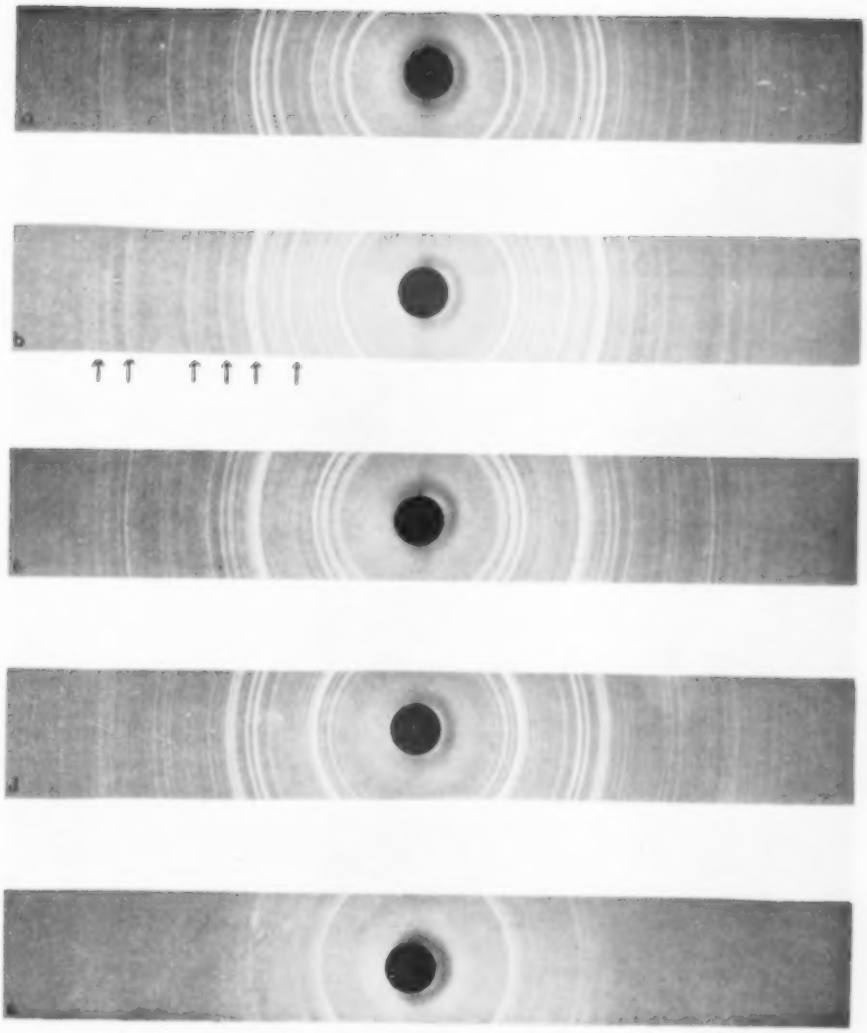

FIG. 1.—X-ray powder photographs of phosphorus sulphides: (a) P_4S_7; (b) The new phase; (c) P_4S_5; (d) P_4S_3 (low temperature form); (e) P_4S_3 (high temperature form).

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The wide composition range over which the phase separates without detectable contamination and the evidence that crystallization of melts is associated with a segregation which does not markedly influence the powder pattern suggest that the product may be of variable composition. Careful measurement of the powder lines from samples of differing composition supported this interpretation. As the sulphur content of the melts fell from $P_4S_{6\cdot75}$ to $P_4S_{5\cdot5}$ the spacings of the powder lines increased reproducibly by an average of about 1 per cent (Table 1). Lattice dimensions

TABLE 1

Composition or origin of sample	Diameters[a] of X-ray powder rings from new phase					
$P_4S_{6\cdot9}$[b]	4·920	6·257	7·194	8·352	10·492	11·548
$P_4S_{6\cdot75}$	4·896	6·235	7·176	8·324	10·484	11·544
$P_4S_{6\cdot75}$[c]	4·900	6·231	7·172	8·322	10·482	11·543
$P_4S_{6\cdot5}$	4·923	6·254	7·195	8·351	10·489	11·571
P_4S_6 Larger crystals	4·906	6·239	7·180	8·337		11·570
P_4S_6 Residue[d]	4·97	6·30	7·22			
$P_4S_{5\cdot5}$	4·947	6·290	7·248	8·389		10·533
P_4S_5	4·963	6·305	7·253	8·423		10·567
P_4S_5[e,f]	4·950	6·288	7·240	8·401	10·557	
P_4S_5[e,f]	4·973	6·301	7·265	8·420	10·565	
P_4S_5[e,g]	4·972	6·291				
Extract from crystals[f]	5·004	6·328	7·255		10·576	
Sulphide from $PCl_3 + H_2S$	4·93	6·26	7·21	8·35		11·63

(*a*) The lines measured are marked by arrows in Fig. 1. The values given (cm) are averages of not less than three measurements. Corrections applied for film "shrinkage" were negative and not greater than 0·05 per cent, except for "Residues from P_4S_6" (0·16 per cent) and "Sulphide from $PCl_3 + H_2S$" (0·10 per cent). (*b*) Contains P_4S_7. (*c*) A second photograph of the preceding sample. (*d*) After removal of most of the crystals. (*e*) A trace of iodine was added to the sample, since this seemed to hasten crystallization. (*f*) Different sample from the preceding. (*g*) In a sealed tube at 170°.

therefore decrease with decreasing sulphur content. Photographs of mechanical mixtures of samples high and low in sulphur gave somewhat diffuse lines as would be expected if the overlap of the diffraction patterns was not exact.

Temperature stability of the new phase

Evidence was found that the new phase is stable only between 200 and 250°. Crystals of composition close to $P_4S_{6\cdot5}$ show visible melting at 250° and become completely liquid at 290–295°. The phase is re-formed when the liquid crystallizes. If, however, the compound is partially melted by heating to 270° and cooled quickly the phase present is P_4S_7, thus confirming that melting occurs with decomposition. Melts of composition straddling the requisite range ($P_4S_{6\cdot75}$–$P_4S_{5\cdot5}$ approx.) almost always supercool to temperatures below 250°. Consequently the new phase rather than P_4S_7 is normally produced. In only two instances out of about fifty did a melt of composition P_4S_6 spontaneously yield P_4S_7 rather than the new phase. On the other hand crystallization of a liquid of composition P_4S_6 to give P_4S_7 was found to occur on seeding at 280° with either P_4S_7 or with the new phase.

The lower temperature limit of stability of the phase lies slightly above 200° but

in practice this does not impose a strict limit upon the range of existence of the new sulphide, or even upon its crystallization from the liquid. Within the temperature range 200–100° decomposition of the crystalline phase to P_4S_7 and P_4S_3 is sufficiently slow to enable it to be obtained in good yield even though cooling over this range may have taken an hour or so. Nevertheless decomposition was found to be largely complete within 24 hr at 195° and within 15 hr at 120°. Thereafter the decomposition occurs progressively more slowly with falling temperature until at ordinary temperature it occurs only over several months. Although the crystalline phase is unstable below 200° it continues to be formed from melts which supercool to 180° or lower before crystallization becomes visible. It must be assumed that at these temperatures the molecular species within the liquid have not reached equilibrium before crystallization occurs. The difficulties in ensuring attainment of equilibrium and in determining the new sulphide in admixture with other sulphides discouraged closer study of its field of existence in the temperature–composition diagram.[11]

Phosphorus pentasulphide was found to decompose to P_4S_7 and P_4S_3 at the eutectic temperature of 130°, and not to melt incongruently at 170° as previously believed.[8] Its stability region is therefore not bounded by the melting point curve. When a melt from P_4S_5 is allowed to cool slowly the new phase is produced.

Behaviour of the new phase with carbon disulphide

Treatment of crystals in a sealed tube at 170° caused crystallization of needles of P_4S_7 and yellow nodules of P_4S_5 as the solution cooled (Table 3). Material recovered from the solution gave the powder pattern of the original crystals, but with the slight expansion characteristic of a reduced sulphur content (Table 1). The result was similar when the crystals were extracted under reflux. Extraction of samples of total composition $P_4S_{5\cdot9}$ rather than of P_4S_{6+} gave an increased proportion of P_4S_3.

It was found that although the new phase is largely decomposed in carbon disulphide even under reflux, the interconversion of P_4S_3, P_4S_5 and P_4S_7 under these conditions is so slight as not further to complicate extraction evidence on the constitution of unknown samples. Interconversion of these three sulphides does, however, occur in solution at 170°.

The sulphide from phosphorus trichloride and hydrogen sulphide

Extraction of this sulphide under reflux has been found[9] to yield P_4S_7 and a soluble fraction, which latter after recovery and re-extraction gave further P_4S_7. This behaviour matches the properties of the new phase, although successive small deposits of P_4S_7 are also produced from P_4S_5. A sample of sulphide prepared from phosphorus trichloride in the same way by the present authors gave the diffraction pattern of the new phase, with line spacings indicative of an intermediate sulphur content (Table 1). There were no lines from other crystalline constituents, but there was considerable diffuse scattering characteristic of amorphous or microcrystalline material on whose constitution no evidence is available. The differing characteristics of the X-ray photographs of the products from the two laboratories suggest that a slight variation in reaction conditions might influence the constitution of the product, and particularly since the new phase is not strictly stable at ordinary temperature. Variation in the proportion of crystalline material could also be expected.

[11] J. E. RICCI advised the authors of the schematic form of the diagram. Private communication 28 May 1959.

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The product from red phosphorus and sulphur

The heptasulphide was the only constituent identifiable in powder photographs of samples of total composition P_4S_6 obtained by firing the elements. The new phase is also present in these samples to a small extent, its presence being revealed by vacuum sublimation. At 100° P_4S_3 distils freely and a small band of the less volatile new phase collects behind it. Extraction with carbon disulphide also removes P_4S_3, along with P_4S_5. No close assessment of the relative proportions of these lower sulphides was attempted owing to the difficulty of their separation and of obtaining a fully crystalline residue from the extract.

Solidification of these sulphide melts occurs largely at 270–250°, above the upper temperature limit of stability of the new phase. This would greatly reduce its formation. The lack of photographic evidence of its presence places the upper limit at perhaps 15 per cent. It is suggested that the relatively high solidification temperature is connected with the presence in the melt of a finely dispersed black solid which promotes nucleation. This solid, possibly unreacted phosphorus and amounting to about 0·2 per cent of the sample weight, was isolable by exhaustive extraction. Addition to the reaction mixture of a trace of iodine, which catalyses the reaction between P_4S_7 and phosphorus, eliminated this black constituent.

It is considered unlikely that P_4S_5 is itself a constituent of the original sample, but rather it is formed through decomposition of the new phase during the extraction. The pentasulphide is unstable above 130°, at which temperature the greater proportion of the material has crystallized. No evidence was found for spontaneous formation of P_4S_5 from other melts, or from P_4S_3 and P_4S_7 at the boiling point of carbon disulphide.

The conclusion made by TREADWELL and BEELI[8] that P_4S_5 was present in a sample of P_4S_6 (presumably obtained from red phosphorus and sulphur) was based on the composition of the soluble extract. The present evidence indicates that this interpretation requires revision.

Concluding remarks

Although the composition range of the newly identified phase includes P_4S_6, its existence would hardly explain the early reports of a sulphide of this stoicheiometric composition as the product from red phosphorus and sulphur. On the other hand the variable composition of the phase, its small temperature range of stability and its sensitivity to solvents and vacuum sublimation would have afforded the evidence considered by other investigators to weigh against the existence of any compound whatever in this composition region.

The non-existence of a stoicheiometric sulphide P_4S_6 structurally analogous to P_4O_6 would not be surprising. If phosphorus were to develop the valence angle of 100° characteristic of its combination with three sulphur atoms, the valence angle of sulphur would be 126°. This is decisively greater than the largest value (108°) found for the angle PSP in any of the known phosphorus sulphides[12–15]. Knowledge of

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[13] Y. C. LEUNG, J. WASER, S. VAN HOUTEN, A. VOS, G. A. WIEGERS and E. H. WIEBENGA, *Acta Cryst.* **10**, 574 (1957).
[14] A. VOS and E. H. WIEBENGA, *Acta Cryst.* **8**, 217 (1955).
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the structural motif underlying the existence of the new phase must await the results of a complete X-ray analysis with which it is hoped to proceed.

EXPERIMENTAL

Preparation of sulphides. P_4S_3[16] and P_4S_7[17] were prepared by firing red phosphorous and sulphur as recommended by STOCK and co-workers. The trisulphide, m.p. 170–172°, was extracted with benzene and pumped free from solvent under high vacuum. The heptasulphide was twice extracted with carbon disulphide. Its melting range, 304–310°, seems characteristic and not due to impurity.

The pentasulphide was prepared by BOULOUCH's method.[7] An atmosphere of carbon dioxide was used to prevent oxidation. The product was recrystallized from carbon disulphide.

Sulphide samples of total composition P_4S_6 were obtained by firing the elements under carbon dioxide in open tubes. A sample from a sealed tube held at 450° for 12 hr was of similar constitution.

Sulphur was redistilled. Reagent grade red phosphorus was boiled with water, washed thoroughly and dried under vacuum. Carbon disulphide was dried over phosphoric oxide and distilled shortly before use.

The new phase. To obtain crystals sufficiently large (3–5 mm) for hand sorting, melts of composition P_4S_6 were made up from P_4S_3 and sulphur, or from P_4S_3 and P_4S_7. The melts were held at 320° for at least 30 min to ensure equilibrium and cooled to room temperature over 5 hr. All heat-treatments were made in sealed tubes from which air had been flushed with carbon dioxide.

It was not possible to select and analyze individual crystals from melts of composition differing much from P_4S_6. Melts containing more sulphur crystallized rapidly to a brittle mass. Those having less sulphur gave a viscous liquid which solidified only slowly at room temperature. Inclusion of a trace of iodine improved crystallization somewhat.

X-ray powder photographs. These were taken with a Philips 114·83 mm camera using $K\alpha$ radiation from copper, or iron for higher resolution. Diffractograms were also run on reference samples. Superposition of these records showed the relative positions of the stronger lines from different sulphides and aided identification of the lines produced by mixtures.

To obtain photographs of the weak pattern of the high temperature form[13,15] of P_4S_3 the sulphide was heated to 100° in the Lindemann tube. Conversion of P_4S_3 to its high temperature form was helpful in revealing the other constituents of mixtures.

Measurement of ring diameters was made on a Hilger and Watts vernier rule. The *d* values of lines from the various sulphides are given in Table 2.

Analysis of the new sulphide by vacuum sublimation. The powdered sample was first decomposed to P_4S_3 and P_4S_7 by heating to 120° in a sealed tube for two days. It was then spread thinly in a porcelain boat and placed in the high vacuum apparatus. At 100° the P_4S_3 sublimed within 30 min. It was checked that more prolonged heating under vacuum caused negligible further loss in weight and that the residue contained no sulphides (such as P_4S_3 or P_4S_5) which were readily extractable with carbon disulphide. In a typical experiment 0·2055 g of sample lost 0·0158 g of P_4S_3.

Solvent extraction. In the reflux method the sample was extracted from a glass "filter thimble" using about 20 ml of solvent. The P_4S_7 which re-crystallized (almost quantitatively due to its low solubility[18]) was weighed (Table 3). Similarly in the sealed tube extractions of the new phase the entire sample was dissolved and cooled slowly to room temperature to produce well developed needles of P_4S_7 for weighing. The solubility of P_4S_3 in carbon disulphide is only about 0·4 g per 100 g at 17°, and since the sulphide crystallizes in characteristic nodules,[19,20] it was possible to separate it by careful concentration of the extracts under a stream of carbon dioxide. The solvent was then removed completely and the residue photographed.

Extraction under reflux of 4·94 g of a typical sample of total composition P_4S_6 obtained by firing red phosphorus and sulphur gave 3·44 g of P_4S_7, 0·29 g of P_4S_5 and about 0·025 g of black residue. The greater portion (1·15 g) of the lower sulphides was extracted in 50 min, but complete extraction of P_4S_7 required two days.

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TABLE 2.—*d* VALUES OF X-RAY POWDER LINES

P_4S_7	P_4S_5	P_4S_3 Low temp. form	P_4S_3 High temp. form	New phase[c]
6·19 *s*	6·11 *m*	6·33 *w*	5·34 *mw*	6·32 *mw*
5·25 *m*	5·87 *m*	5·71 *m*	5·18 *s*	5·72 *s*
5·01 *w*	5·32 *s*	5·30 *w*	4·91 *m*	5·14 *mw*
4·79 *w*	5·15 *s*	4·93 *s*	4·70 *w*	4·68 *m*
4·59 *w*	4·77 *s*	4·62 *mw*	4·07 *w*	4·32 *m*
4·37 *m*	7 lines[a]	4·39 *w*	3·07 *w*	3·62 *ms*
3·90 *mw*	3·14 *s*	4·17 *w*	2·90 *w*	3·31 *m*
3·34 *m*[b]	3·08 *s*	3·43 *mw*		3·17 *m*
3·13 *w*	3·02 *m*	3·14 *s*		2·95 *ms*
3·09 *ms*	4 lines[a]	2·99 *ms*		2·86 *s*
3·04 *w*	2·74 *w*	2·78 *mw*		3 lines[a]
2·92 *s*	2·69 *m*	2·73 *mw*		2·49 *m*
3 lines[a]	2·59 *m*[b]	2·69 *m*		3 lines[a]
2·66 *m*	2·43 *m*	6 lines[a]		2·16 *mw*
2·57 *w*	2 lines[a]	2·09 *mw*		1·74 *mw*
2·42 *w*	2·17 *w*[b]	2·05 *mw*		1·65 *w*[b]
2·30 *mw*	2·07 *w*	1·98 *mw*		1·59 *w*
2 lines[a]	2·00 *mw*	3 lines[a]		
2·14 *m*	4 lines[a]	1·80 *mw*		
1·99 *ms*	1·78 *ms*	2 lines[a]		
9 lines[a]	1·74 *mw*	1·71 *w*		
1·62 *m*	1·68 *w*	1·65 *mw*		
	1·63 *w*			

s = strong; *ms* = medium to strong; *m* = medium; *mw* = weak to medium; *w* = weak.
[a] Unmeasured lines. [b] Broad line. [c] Crystals from a P_4S_6 melt.

TABLE 3.—EXTRACTION OF NEW PHASE

Sample (g)		Procedure	P_4S_7 recovered (g)	Sulphides identified in extract
Crystals from P_4S_6 melt	0·1932	Reflux	0·147	New phase, P_4S_5
	0·2042	Sealed tube at 170°	0·154	New phase, P_4S_5 (0·014 g)
Sample of total composition $P_4S_{5\cdot0}$	1·6657	Reflux	1·164	New phase, P_4S_3, P_4S_5
	1·1165	Sealed tube at 170°	0·752	New phase, P_4S_3, P_4S_5 (0·093 g)

The black residue from "P_4S_6". This residue was extracted with water to remove oxidized material but still contained 7 per cent sulphur. The strongest powder lines have *d* values 4·29 (*m*), 3·34 (*s*), 1·82 (*m*), 1·54 (*m*), 1·39 (*m*). These do not correspond to red[21] or black[22] phosphorus, but the variability of the former is such that the possibility of the material being an impure form of the element cannot be excluded.

Interactions of phosphorus sulphides in carbon disulphide. Under reflux 0·4091 g P_4S_7 and 0·2583 g P_4S_3 were heated for two days (both sulphides being placed in the extraction thimble initially). The recovery of 0·393 g P_4S_7 indicates little or no reaction. However, when 0·2865 g P_4S_7 and 0·1810 g P_4S_3 were heated to 170° with 7 ml of solvent in a sealed tube 0·092 g P_4S_8 and only 0·120 g P_4S_7 crystallized from the solution.

When 0·3157 g P_4S_3 was heated with solvent at 170° it gave 0·110 g P_4S_7. Under reflux for two days 0·4460 g P_4S_8 gave 0·040 g P_4S_7. Likewise 0·2430 g P_4S_8 with 0·2980 g P_4S_7 deposited 0·326 g P_4S_7 under the same conditions.

The reaction between phosphorus trichloride and hydrogen sulphide. Reaction between equivalent proportions of the chloride and hydrogen sulphide (initial pressure 2 atm in the sealed tube) was allowed to proceed for a week at ordinary temperature. Flocculent sulphide slowly separated within the liquid. It was pumped free from volatile material before photographing.

Analysis. This was done gravimetrically as recommended by BEELI[23], but using a temperature of 170° for the nitric acid oxidation.

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THE INTERACTION OF BORON HALIDES WITH SILYL CYANIDES*

E. C. Evers, W. O. Freitag, W. A. Kriner, A. G. MacDiarmid and S. Sujishi

John Harrison Laboratory of Chemistry, University of Pennsylvania, and the Department of Chemistry, Illinois Institute of Technology

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Abstract—Boron halides do not react with SiH_3CN and $(CH_3)_3SiCN$ to form stable addition compounds such as those formed between boron halides and alkyl and aryl cyanides. Instead, reaction occurs at low temperatures to form unstable addition compounds which spontaneously decompose with the elimination of silyl halide and the formation of a solid residue of general formula $(BX_2CN)_n$.

Alkyl and aryl cyanides have been reported to react with BF_3 and BCl_3 to form addition compounds of the type $RCN{\cdot}BX_3$, e.g. $CH_3CN{\cdot}BF_3$,[1,2] $CH_3CN{\cdot}BCl_3$,[2] $C_6H_5CN{\cdot}BF_3$,[1] $C_6H_5CN{\cdot}BCl_3$,[3] etc. They are generally white solids which decompose on heating to reform the organic cyanide and the boron halide. In the vapour state they are usually completely dissociated. Infra-red studies on the BCl_3 derivatives indicate that the structure of the addition compounds is $RC{\equiv}N : BCl_3$ rather than $RCCl{=}N_2ClB$.[4]

The present investigation was carried out in order to ascertain whether the Si—CN linkage in SiH_3CN and $(CH_3)_3SiCN$ would react with boron halides in an analogous manner to the C—CN linkage in alkyl and aryl cyanides. Whether silicon cyanides have the normal or isocyanide structure or whether they are equilibrium mixtures of the normal and iso forms is still somewhat questionable.[5] For the lack of good evidence to the contrary the normal structure has been assumed for the silicon cyanides discussed in this communication.

EXPERIMENTAL

Materials. SiH_3CN and $(CH_3)_3SiCN$ were prepared according to procedures described in a previous paper[6] and were of a similar state of purity. Commercial BF_3,† BCl_3‡ and BBr_3‡ were used after suitable purification.

Reaction of SiH_3CN *with* BF_3. SiH_3CN (1·85 mmoles) and BF_3 (3·03 mmoles) were combined at

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† The Matheson Company, Inc.

‡ American Potash and Chemical Corp.

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−196° and held at −78° for 1 hr. The volatiles were removed at −78° and were found to be BF_3 (1·65 mmole. Mol. wt.—Found: 68·7. Calc. 67·8. Confirmed by infra-red spectrum[7]).

Since a trace of SiH_3F was observed in the spectrum of the BF_3 it was concluded that decomposition of any adduct formed was occurring slowly at −78°. Consequently no further time was allowed for the solid-gas reaction between SiH_3CN and BF_3 and the reaction vessel was warmed to room temperature. On distillation, unreacted SiH_3CN (0·46 mmole. Mol. wt.—Found: 57·0. Calc. 57·1) was found in the volatiles. The SiH_3CN/BF_3 ratio in the solid was calculated to be 1·01. The reaction occurring can be represented by the equation

$$SiH_3CN + BF_3 \rightarrow SiH_3CN{\cdot}BF_3 \quad (1)$$

The only volatile product found from the decomposition of the adduct, which occurred rapidly at room temperature, was SiH_3F (1·37 mmole. Mol. wt.—Found: 48·6. Calc. 50·1. Confirmed by infra-red spectrum[8]). A non-volatile, yellowish solid remained in the reaction vessel. The empirical composition of this material was calculated to be exactly BF_2CN from the quantities of reactants and products involved. The reaction occurring between −78° and room temperature therefore proceeds quantitatively according to the equation below

$$SiH_3CN{\cdot}BF_3 \rightarrow SiH_3F + \frac{1}{n}(BF_2CN)_n \quad (2)$$

The identity of the $SiH_3CN{\cdot}BF_3$ was confirmed in another experiment, in which 3·23 mmole of adduct of SiH_3CN/BF_3 ratio 1·00 were hydrolysed in 10% KOH solution. (Hydrogen evolved—Found: 9·50 mmole. Calc. 9·70 mmole).

In a similar experiment involving CH_3SiH_2CN and BF_3 it has been reported[9] that the only volatile material isolated was unreacted BF_3 which was identified by its molecular weight (Found: 67·0. Calc. 67·8). Since the molecular weight of CH_3SiH_2F is 64·1 it appears likely, in the light of our observations, that this volatile material may have been CH_3SiH_2F or a mixture with BF_3.

Reaction of $(CH_3)_3SiCN$ *with* BF_3. $(CH_3)_3SiCN$ (2.56 mmole) and BF_3 (3·00 mmole) were combined at −196°, warmed to −126°, and held at this temperature for 1·5 hr. BF_3 (0·471 mmole. Mol. wt.—Found: 68·2. Calc. 67·8) was removed at −126°. The $(CH_3)_3SiCN/BF_3$ reaction ratio was calculated to be 1·01. The vapour pressure of the adduct at −126° was zero. On raising the temperature slowly in the range from −126° to −95° the pressure increased to 20 mm. Analysis of the gas phase at −95° showed only BF_3 (Mol. wt.—Found: 67·0. Calc. 67·8), which was returned to the reaction vessel. On cooling to −126° the pressure returned to zero. On warming to −78° the pressure increased to 100 mm, but, within 3 hr at −78°, the pressure fell to 2 mm. Subsequent heating in the temperature range from −78° to −30° caused a further pressure increase.

A second reaction was carried out at −78° using approximately equimolar quantities of $(CH_3)_3SiCN$, (0·603 mmole) and BF_3, (0·625 mmole). A fairly rapid reaction occurred at this temperature as evidenced by a rapid fall in the total pressure of the reactants within a few minutes. The mixture was allowed to stand at −78° for 16·5 hr (final pressure observed, 5 mm), and all substances volatile at this temperature were then removed. The gas recovered consisted only of excess BF_3 (0·022 mmole) giving a $(CH_3)_3SiCN/BF_3$ ratio of 1·00 in the solid residue.

In a third experiment, using 2·43 mmole of adduct (Calc. $(CH_3)_3SiCN/BF_3$ ratio: 0·990), the observations reported above were confirmed. Analysis of the vapour phase at −32° showed only $(CH_3)_3SiF$ (Found: 2·25 mmole. Calc. 2·43 mmole. Mol. wt.—Found: 90·4. Calc. 92·2). This represents a 92·6 per cent yield of $(CH_3)_3SiF$ if decomposition of the addition compound proceeds according to equation (5). The residue therefore had the approximate empirical composition BF_2CN.

The results may be interpreted as follows: in the temperature range from −126° to −95° reversible dissociation is occurring according to the equation:

$$(CH_3)_3SiCN{\cdot}BF_3(s) \rightleftarrows (CH_3)_3SiCN(s) + BF_3(g) \quad (3)$$

On standing at −78° it is suggested that the adduct rearranges in the solid state as follows:

$$(CH_3)_3SiCN{\cdot}BF_3(s) \rightarrow (CH_3)_3SiF{\cdot}BF_2CN(s) \quad (4)$$

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Such a rearrangement would shift the equilibrium [equation (3)] to the left thus accounting for the decrease in pressure. Heating from −78° to −30° then causes elimination of $(CH_3)_3SiF$, leaving $(BF_2CN)_n$ as residue, as shown below

$$(CH_3)_3SiF{\cdot}BF_2CN \rightarrow (CH_3)_3SiF + \frac{1}{n}(BF_2CN)_n \quad (5)$$

Adduct formation between $(CH_3)_3SiF$ *and* BF_3. $(CH_3)_3SiF$ (1·314 mmole). Vapour pressure at −78°—Found: 3·0 mm. Literature value:[10] 3·4 mm), which was prepared by the decomposition of $(CH_3)_3SiCN{\cdot}BF_3$, and BF_3 (5·30 mmole) were combined at −196°. The mixture was then brought to zero pressure at −126° by removing materials volatile at this temperature. BF_3 (4·07 mmole) and a trace of $(CH_3)_3SiF$ were obtained. The entire sample was allowed to vapourize completely and consisted of 2·48 mmole of gas. The $BF_3/(CH_3)_3SiF$ ratio in the solid was calculated to be 0·984. The saturation pressure at −95° was 20 mm, and at −78°, 100 mm.

A similar experiment was carried out with $(CH_3)_3SiCl$ and BCl_3. No evidence of adduct formation was found in the temperature range −78° to −46°.

Thermal decomposition of $(BF_2CN)_n$. To hasten the decomposition which proceeded slowly at room temperature a freshly prepared sample of $(BF_2CN)_n$ (3·14 mmole) was heated to 50° for 2 hr. BF_3 (0·46 mmole. Mol. wt.—Found: 68·0. Calc. 67·8) was obtained. Heating to 100° for 7 hr and 200° for 2 hr liberated more BF_3 (1·32 mmole; identified by infra-red spectrum[7]). Additional heating at 300° for 6 hr produced 0·20 mmole of gas assumed to be BF_3. Total BF_3 recovered was 1·98 mmole.

A black, solid residue remained which, by calculation, had an approximate composition of BC_3N_3. It showed weak infra-red absorption in the C≡N region at 2230 cm^{-1} but differed from the $B(CN)_3$ reported by CHAIGNEAU[11] in its colour and lack of volatility.

Reaction of SiH_3CN *with* BCl_3. SiH_3CN (1·82 mmole) and BCl_3 (2·16 mmole) were combined at −196° and kept at −78° for 18 hr. The volatiles were removed at −78° and on fractionating yielded BCl_3 (0·343 mmole. Mol. wt.—Found: 118. Calc. 117) and SiH_3Cl (0·96 mmole. Mol. wt.—Found: 66·9. Calc. 66·5. Confirmed by infra-red spectrum[12]). The adduct was presumed to have partly decomposed at −78° during the relatively long reaction time. The SiH_3CN/BCl_3 reaction ratio was calculated to be 1·00. The reaction occurring can be represented by the equation

$$SiH_3CN + BCl_3 \rightarrow SiH_3CN{\cdot}BCl_3 \quad (6)$$

Decomposition of the adduct was brought to completion by holding it at room temperature for 1 hr; the residue was a yellow solid. Fractionation of the volatiles yielded only SiH_3Cl (0·79 mmole. Mol. wt.—Found: 67·0. Calc. 66·5). Total SiH_3Cl recovered was 1·75 mmole.

This represents a 96·3 per cent yield of SiH_3Cl if decomposition proceeds according to the equation

$$SiH_3CN{\cdot}BCl_3 \rightarrow SiH_3Cl + \frac{1}{n}(BCl_2CN)_n \quad (7)$$

The residue therefore had the approximate empirical composition BCl_2CN.

The residue, when heated for 1·5 hr, followed by gentle flaming generated BCl_3 (1·09 mmole. Mol. wt.—Found: 117. Calc. 117. Confirmed by infra-red spectrum[13]). The solid remaining had an empirical composition approaching BC_2N_2 but contained some chlorine.

Reaction between $(CH_3)_3SiCN$ *and* BCl_3. $(CH_3)_3SiCN$ (3·52 mmole) and BCl_3 (5·45 mmole) were combined at −196° and held at −78° for 18 hr. The volatiles were removed at −78° and on fractionating yielded only BCl_3 (2·40 mmole. Mol. wt.—Found: 117. Calc. 117. Confirmed by infra-red spectrum[13]). The temperature was then raised to 0° and the volatile material was found to consist only of $(CH_3)_3SiCN$ (0·490 mmole. Mol. wt.—Found: 98·2. Calc. 99·2. Vapour pressure at 23°—Found: 17·5 mm. Literature value[6] 17·3 mm). The $(CH_3)_3SiCN/BCl_3$ ratio in the yellow-white solid residue was calculated to be 0·994. The solid was heated at 50–55° for 6 hr during which time 2·28 mmole of volatile material was formed. Additional heating at 90–99° for 2·5 hr yielded 0·635

[10] H. S. BOOTH and J. F. SUTTLE, *J. Amer. Chem. Soc.* **68**, 2658 (1946).
[11] M. CHAIGNEAU, *C.R. Acad. Sci., Paris* **239**, 1220 (1954).
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[13] R. E. SCRUBY, J. R. LACHER and J. D. PARK, *J. Chem. Phys.* **19**, 386 (1951).

mmole of volatiles and further heating at 180–200° for 3 hr yielded an additional 0·885 mmole of volatile material. Fractionation of the combined volatiles gave $(CH_3)_3SiCl$ (2·90 mmole. Mol. wt.—Found: 109. Calc. 109. Identified by infra-red spectrum[14]) and BCl_3 (0·900 mmole. Mol. wt.—Found: 117. Calc. 117. Identified by infra-red spectrum[13]). The residue was a black powder which was partly soluble in water, giving a brownish black suspension.

A 95·7 per cent yield of $(CH_3)_3SiCl$ was obtained, assuming that reaction occurs according to the equation below

$$(CH_3)_3SiCN + BCl_3 \rightarrow (CH_3)_3SiCN{\cdot}BCl_3 \rightarrow (CH_3)_3SiCl + \frac{1}{n}(BCl_2CN)_n \quad (8)$$

The postulated material, $(BCl_2CN)_n$, is partly decomposed during the reaction with the liberation of BCl_3.

Reaction of $(CH_3)_3SiCN$ *with* BBr_3. BBr_3 (2·95 mmole. Vapour pressure at 9°—Found: 30·0 mm. Literature value:[15] 30·0 mm) and $(CH_3)_3SiCN$ (2·87 mmole) were combined at −196° and brought to −40° at which temperature there was no measurable pressure. The temperature was allowed to rise to 25° over a period of 5 hr; the white solid gradually darkened, but did not melt. After standing for 24 hr at room temperature, 1·31 mmole of a mixture of gases of mol. wt. 164 was obtained which was calculated to consist of $(CH_3)_3SiBr$ (1·16 mmole) and BBr_3 (0·15 mmole). After standing for five days at room temperature $(CH_3)_3SiBr$ (0·61 mmole. Mol. wt.—Found: 155. Calc. 153. Vapour pressure—43 mm and 30 mm at 8·0° and 0°, respectively. Extrapolated b.p.—Found: 83°. Literature value:[16] 80–81°) was obtained and the solid residue had turned black. On heating the residue to 50–60° for 1 hr, and 100° for 2 hr, two fractions consisting of a mixture of $(CH_3)_3SiBr$ and BBr_3 were obtained (Fraction No. 1, 0·7 mmole, mol. wt. 171; fraction No. 2, 0·45 mmole, mol. wt. 167). It was calculated that approximately one mmole of $(CH_3)_3SiBr$ was present in the two fractions taken together.

The over-all reaction occurring can be represented by the equation below

$$(CH_3)_3SiCN + BBr_3 \rightarrow (CH_3)_3SiBr + \frac{1}{n}(BBr_2CN)_n \quad (9)$$

The yield of $(CH_3)_3SiBr$ based on the $(CH_3)_3SiCN$ consumed is approximately 98 per cent.

CONCLUSION

The over-all reaction of boron halides with silyl cyanides has been found to differ from that reported for alkyl and aryl cyanides. With silyl cyanides, reaction has been found to occur at low temperatures with the formation of unstable addition compounds which spontaneously decompose to form the silyl halide and nonvolatile, presumably polymeric solids of general composition BX_2CN as indicated in the equation below

$$R_3SiCN + BX_3 \rightarrow R_3SiCN{\cdot}BX_3 \rightarrow R_3SiX + \frac{1}{n}(BX_2CN)_n \quad (10)$$

where R=H or CH_3 and X=F, Cl or Br. The compounds $(BX_2CN)_n$ spontaneously decompose with the liberation of boron halides and only in the case of the fluoride is the material sufficiently stable to allow isolation of pure $(BF_2CN)_n$.

The reactions described in equation (10) are entirely analagous to those described in a previous paper[6] for silyl cyanides and B_2H_6 (where X=H in the above equation). In the case of the boron halides, the species $R_3SiCN{\cdot}BX_3$ and $(BX_2CN)_n$ are much less stable thermally and could not therefore be completely characterized.

[14] A. L. SMITH, *J. Chem. Phys.* **21**, 1997 (1953).
[15] A. STOCK and E. KUSS, *Ber. Dtsch. Chem. Ges.* **47**, 3113 (1914).
[16] P. A. MCCUSKER and E. L. REILLY, *J. Amer. Chem. Soc.* **75**, 1583 (1953).

The difference in behaviour of boron halides with either alkyl or aryl cyanides and silyl cyanides appears to be due primarily to the fact that in the case of silicon, the vacant 3*d* orbitals greatly facilitate the transfer of a halogen from the boron to the silicon with the subsequent elimination of silyl halide. With the alkyl and aryl cyanides, reversible dissociation of the addition compounds occurs before halogen transfer can take place.

Acknowledgement—The authors are indebted to Mr. J. A. MARLEY for carrying out the experiments on the interaction of BF_3 with $(CH_3)_3SiCN$.

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A NEW COMPLEX URANIUM COMPOUND, $5UCl_5 \cdot CCl_2{=}CCl{-}COCl$* (PENTA-URANIUM PENTACHLORIDE, TRICHLOROACRYLYL CHLORIDE)

R. E. PANZER‡ and J. F. SUTTLE§

(*Received* 14 *July* 1959)

Abstract—A dark red co-ordination compound of uranium, $5UCl_5 \cdot CCl_2{=}CCl{-}COCl$ is reported. The material is the primary reaction product from uranium trioxide and hexachloropropene. It is readily dechlorinated to form uranium tetrachloride, trichloroacrylyl chloride and chlorine. The material is probably triclinic. Indices of refraction are greater than 1·600. The compound melts at 96°C (closed tube) without decomposition. The compound could not be separated into uranium pentachloride and the organic portion without decomposing the UCl_5. Ionizing nonaqueous solvents dissolve it readily and it reacts with PCl_5 in phosphorus oxychloride to form $UCl_5 \cdot PCl_5$. A structure is postulated in which a molecule of UCl_5 is co-ordinated to each of the five available chlorine or oxygen atoms of trichloroacrylyl chloride.

NUMEROUS methods and reagents have been utilized for the chlorination of uranium oxides. A review of the subject has been published by KATZ and RABINOWITZ.[1] The use of hexachloropropene as a chlorinating agent has proved to be one of the easier and more efficient methods.[2,3,4]

MILLER and DEAN[4] list the following reactions in explanation of the formation of the various products in the reaction of hexachloropropene and uranium trioxide.

$$UO_3 + 3CCl_2{=}CCl{-}CCl_3 \rightarrow UCl_5 + 3CCl_2{=}CCl{-}COCl + \tfrac{1}{2}Cl_2 \quad (1)$$

$$UCl_5 \rightarrow UCl_4 + \tfrac{1}{2}Cl_2 \quad (2)$$

$$C_3Cl_6 + Cl_2 \rightarrow CCl_4 + C_2Cl_4 \quad (3)$$

$$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6 \quad (4)$$

$$2UO_3 + \tfrac{13}{2}Cl_2 \rightarrow 3ClO_2 + 2UCl_5 \quad (5)$$

Since the initial reaction, equation (1), produces uranium pentachloride it was hoped that this procedure might be used as a method of obtaining pure UCl_5 for use in the study of the compound, $UCl_5 \cdot PCl_5$.[5]

The procedure[3] was modified to prevent the reaction from going to the uranium tetrachloride stage.

When the initial reaction started the electric mantle supplying the necessary heat to initiate the reaction was removed. The exothermic reaction then proceeded rapidly

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‡ Present address: U.S. Naval Ordnance Laboratory, Corona, California.

§ Present address: Ernest O. Lawrence Radiation Laboratory, Berkeley, California.

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[4] A. J. MILLER and L. B. DEAN, U.S.A.E.C., AECD-4179 (1946).

[5] R. E. PANZER, Doctoral Dissertation, University of New Mexico (1958).

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to completion. At this point the hot reaction mixture was filtered through a coarse fritted glass filter stick into a dry flask, tightly stoppered and allowed to cool. This deviation reduces the amount of uranium tetrachloride to a minimum.

After cooling, the dark red reaction mixture was examined and found to have a large mass of dark red acicular crystals covering the bottom of the 1 l. flask to a depth of several centimeters. The supernatant liquid was decanted from the crystals and cooled further in a refrigerator at 0°C. An additional batch of finer crystals was thus obtained. The crystals were transferred in a dry box and dried for 24 hr at a pressure of 1 μ and a temperature no greater than 50°C.

The resulting material had a strong characteristic odour of trichloroacrylyl chloride, the principal by-product of the reaction indicated by equation (1). Treatment of a weighed portion of the dark red needles with 3 N sulphuric acid caused an oily material to separate in a well defined layer. The uranium portion of the compound dissolved in the acidic solution to form a green aqueous solution of tetravalent uranium. The organic layer was recovered quantitatively and its boiling range determined to be 155–158°C. This is the boiling range of trichloroacrylyl chloride. Analysis of the red compound gave the following results: U, 52·4; Cl, 39·1 (water soluble chloride); organic portion, 8·62%. Consideration of the data obtained indicate that the formula of the dark red compound is $5UCl_5$·trichloroacrylyl chloride. Its theoretical composition is as follows: U, 52·9; Cl, 38·5 (water soluble chloride); organic portion, 8·54%.

Optical properties of the compound were determined by the usual methods. The compound is red-orange in plane polarized light; the axial angle ($2V$) is large, but the sign could not be determined because of a poor interference figure. The material has very low symmetry, probably triclinic. Indices of refraction are greater than 1·600 and birefringence is high, but the interference colours are drastically masked by the colour of the material. The compound is very reactive, especially with index media. When ground in a dry box under nitrogen dried over phosphorus pentoxide, the material was bright red-orange, but changed to a dirty brown before it could be placed in a capillary. Powder X-ray photographs produced no lines from this material.

The dark red complex melts at 96°C in a closed tube. When heated in an evacuated sealed tube it boils at 132°C. There was no evidence of sublimation under those conditions and the material appeared unchanged when cooled.

It was not possible to remove the organic portion of the complex molecule leaving the uranium pentachloride unchanged. The material is very slightly soluble in carbon tetrachloride and appeared to dissolve in benzene, but after a short time a dark brown solid separated from the solution. An extraction with carefully dried benzene produced the same results. The solvent became highly coloured with the brown material which was found to fluoresce a light blue in ultra-violet light. Other solvents appeared to remove the organic portion of the red complex, but the uranium pentachloride was then reduced to uranium tetrachloride.

The only solvents in which the red compound is more than slightly soluble are ionizing nonaqueous solvents such as thionyl chloride or phosphorus oxychloride. In the latter solvent the red compound reacted with phosphorus pentachloride to form the compound, $UCl_5 \cdot PCl_5$.

The absorption spectrum of $5UCl_5$·trichloroacrylyl chloride dissolved in phosphorus

oxychloride is shown in Fig. 1. The usual procedure was followed of taking a blank reading on the pure solvent at each wavelength used.

The investigations previously mentioned,[5] have emphasized the fact that uranium pentachloride always occurs in a co-ordinated structure with some molecule. For example, it is known to exist as the dimer, $(UCl_5)_2$, possibly in the ionic form, $(UCl_6^-)(UCl_4^+)$. It forms the compound $UCl_5 \cdot PCl_5$ which was found to exist as $(UCl_6^-)(PCl_4^+)$. Another compound of the same type is the thionyl chloride

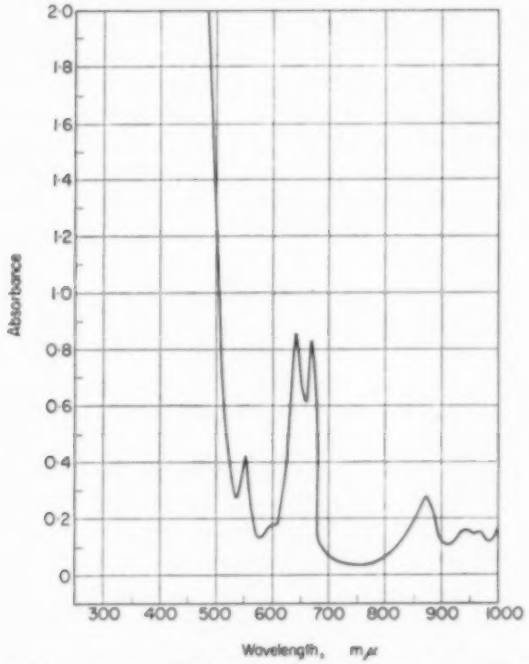
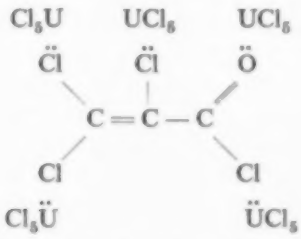


FIG. 1.—Absorption spectrum $5UCl_5$·trichloroacrylyl chloride in phosphorus oxychloride concentration—96·4 g/l. ($4{\cdot}25 \times 10^{-3}$ molar).

compound, $UCl_5 \cdot SOCl_2$, which is thought to be ionized in a similar manner, $(UCl_6^-)(SOCl^+)$.[6]

With this persistent co-ordination of UCl_5 in mind the structure of the dark red compound, $5UCl_5$·trichloroacrylyl chloride is believed to be as follows:



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The presence of the conjugated double bond system would be expected to give rise to a highly coloured stabilized structure in which a number of resonance forms could exist. In contrast, the simple dimeric molecule, $(UCl_5)_2$, is a tan to light brown in colour.

Detailed investigations of the structure of this interesting compound might be of value in elaborating the structures of other complex compounds of uranium pentachloride.

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SOME INNER COMPLEXES OF COBALT (III) WITH DIETHYLENETRIAMINE*

P. H. CRAYTON and J. A. MATTERN‡
Union Carbide Metals Company, P.O. Box 580, Niagara Falls, New York

(*Received* 16 *July* 1959)

Abstract—A series of cobalt complexes containing one molecule of the tridentate diethylenetriamine for each cobalt atom have been prepared: [Co dien $(NO_2)_3$], [Co dien $(NH_3)(NO_2)_2$]Cl, [Co dien $(NO_2)_2Cl$], [Co dien $(SCN)_3$], [Co dien $(SCN)_2OH$], [Co dien Cl_3] and [Co dien $(NO_3)_2$]. The preparation and chemical properties are discussed, pointing out some unusual reactions. Absorption peaks have been determined and compared with similar compounds of known configuration. The preparation of *trans* [Co dien $(NO_2)_2$] from *cis* and *trans* complexes is described and the implication discussed. *Cis*-[Co dien X_2] complexes could not be prepared.

THE tridentate amine, diethylenetriamine, not only provides several interesting structural possibilities for bis complexes (Fig. 1) but also enables the preparation

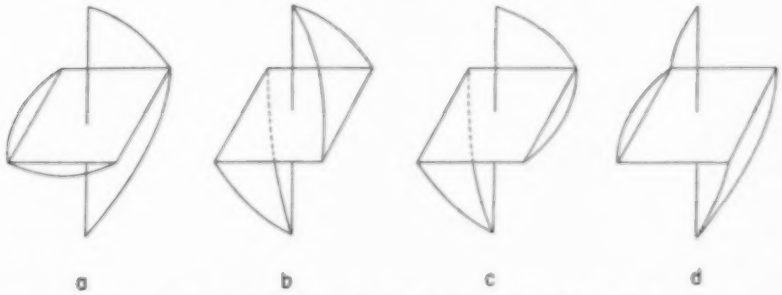

FIG. 1.—Possible structures for bis diethylenetriamine complexes.

of inner complex compounds with trivalent metals (i.e., Co). A *cis* or a *trans* structure, with reference to the position of the central secondary amine group, can be conceived (a, b and c, d). Two *trans* forms can be constructed depending on whether the amine molecule lies in one plane (a) or undergoes a right angle bend in the centre (b). Both structures are allowed from a consideration of bond angles for these groups. A pair of optically active isomers is possible for the *cis* configuration (c, d).

With a single amine molecule occupying three of the six co-ordinate positions of trivalent cobalt, a stable base is obtained which can be used to prepare a number of inner complexes which possess an interesting chemistry.

The purpose of this work was to determine the structure of the bis complex, to try to prepare the structures not normally found, and to prepare cobalt complexes containing one molecule of amine and determine their properties.

* Submitted in partial fulfillment for the Ph.D. degree to the University of Buffalo, Buffalo, New York.
‡ Professor, Dept. Chem. Univ. of Buffalo, Buffalo 14, New York.

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HISTORY

Complexes of two tridentate amines, triphenyl[1,2,3] and α,β,γ-triaminopropane[4,5] have been reported. Structural studies of the bis triaminopropane complex of platinum were conducted by MANN who could find no evidence of a cis configuration.[4]

The bis complexes of diethylenetriamine with cobalt[6] have been known for several years. The preparation and properties of a number of complexes of other metals have been described.[7] The existence of ions containing only one molecule of the amine was demonstrated through absorption spectra of solution by JOB and BRIGANDO,[8,9,10] and NAENDLER.[11]

The first elucidation of a definite configuration, that of the amine lying in a single plane was also described.[12]

EXPERIMENTAL

Preparations

[Co dien$_2$]Cl$_2$. The method outlined by JOB and BRIGANDO was followed.[6] It was observed that no salt would crystallize or precipitate from acid solution.

Trans-[Co(NH$_3$)$_2$(NO$_2$)$_2$]. This compound was prepared by the method described by ERDMAN.[13]

Cis-[Co(NH$_3$)$_2$(NO$_2$)$_2$]. The preparation of this compound has been described by JORGENSEN.[14]

[Co dien (SCN)$_2$OH]. When 20 ml of 10 per cent aqueous solution of diethylenetriamine was slowly added to one made by dissolving 5 g of cobalt nitrate hexahydrate and 5·5 g of potassium thiocyanate, by aeration, a dull red non-crystalline solid separated. The most favourable pH for the preparation was four to six. The precipitate was allowed to stand overnight, then filtered, washed with water and dried in an oven at 110°C. The compound was purified by dissolving in two molar sodium hydroxide then neutralizing the solution. The yield was 3·7 g or 60 per cent. Found: Co, 20·01; C, 24·22; S, 21·60. Calc. for [Co dien (SCN)$_2$OH]: Co, 19·96; C, 24·39; S, 21·72%.

[Co dien (SCN)$_2$]. A solution of 6 ml of diethylenetriamine in 50 ml of absolute alcohol was slowly added to one made by dissolving 10 g of cobaltous thiocyanate and 5 g of potassium thiocyanate in 200 ml of absolute alcohol. A tan precipitate began to form almost immediately. Dry air was bubbled through the solution for 1 hr. The precipitate was filtered with suction and washed with alcohol until the washings were colourless. Care was taken to suck the precipitate dry. A final wash was made with ether and the compound stored in a desiccator. The yield was 18 g or 95 per cent. Found: Co, 17·55; C, 24·90; S, 28·40. Calc. for [Co dien (SCN)$_2$]: Co, 17·5; C, 24·98; S, 28·60%.

[Co dien (NO$_2$)$_2$]. (A) From cobaltous nitrate—A solution was prepared by adding 10·5 g of cobaltous nitrate hexahydrate and 11 g of sodium nitrite to 15 ml of water and adjusting the pH to five to six. Aeration of the solution was begun and a solution of 3 ml of diethylenetriamine in 12 ml of water was added dropwise. The formation of a green precipitate indicated that the amine was added too rapidly or that the pH was too high. After aerating for 1 hr the solution was filtered and the precipitate washed several times with water then with alcohol. The yield was 10·3 g or 78 per cent. Found: Co, 19·50; C, 16·05; N, 27·95. Calc. for [Co dien (NO$_2$)$_2$]: Co, 19·63; C, 15·99; N, 27·99%.

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(B) From *trans*-[$Co(NH_3)_2(NO_2)_3$]—Ten grammes of *trans*-[$Co(NH_3)_2(NO_2)_3$] was dissolved in 15 ml of water by heating. To the hot solution was added 2·5 ml of diethylenetriamine. A stream of air was passed through the solution which was kept at about 60°C for 45–60 min or until the odour of ammonia could not be detected. The solution was allowed to cool causing the crystallization of the complex. This was filtered and washed several times with water and alcohol. The yield was 10 g or 80 per cent.

(C) From sodium cobaltinitrite—Seven grammes of sodium cobaltinitrite was dissolved in 15 ml of water and the solution was heated to 50°C and 2·7 ml of diethylenetriamine was added. A yellow crystalline precipitate formed which grew as the solution cooled. This precipitate was filtered with suction and washed several times with water then alcohol. A second crop of crystals was obtained by concentrating the mother liquor. The yield was 3 g or 59 per cent.

[Co dien $(NO_2)_2Cl$]. This compound was prepared from trinitrodiethylenecobalt(III) by allowing 10 g of this complex to stand 24 hr under 100 ml of 6 N hydrochloric acid. At this point red brown crystals appear under a green solution. The crystals were filtered and washed with warm water until the wash water had only a faint yellow colour. The crystals were dried at 110°C. Eight grammes of crystals were obtained or an 82 per cent yield. Found: Co, 20·50; C, 16·50; N, 14·45; Cl, 12·25. Calc. for [Co dien $(NO_2)_2Cl$]: Co, 20·40; C, 16·60; N, 14·50; Cl, 12·25%.

[Co dien $(NH_3)(NO_2)_2$]Cl. This compound was prepared by replacing the chloro group in dinitrochlorodiethylenetriaminecobalt(III) with ammonia. Five grammes of the dinitrochloro complex was placed in a solution of 25 ml of water and 5 ml of ammonium hydroxide. This was heated nearly to boiling and held there about 30 min at which time the odour of ammonia was faint. The solution was allowed to cool overnight and any unconverted starting material filtered off. The solution was evaporated until crystals began to appear then allowed to cool. The crystals were filtered and washed first with 20 per cent alcohol, then alcohol and dried at 110°C. About 4·5 g of product was obtained or 90 per cent yield. Found: Co, 19·25; N^{-3}, 18·00; Cl, 11·40. Calc. for [Co dien $(NH_3)(NO_2)_2$]Cl: Co, 19·25; N^{-3}, 18·25; Cl, 11·60%.

[Co dien Cl_2]. This compound was prepared by replacing the three nitrito groups in 10 g of the trinitro complex with chloro groups by gently heating with 250 ml of hydrochloric acid until the evolution of NO_2 ceased. This solution was cooled and allowed to stand overnight. Fine brown crystals of trichlorodiethylenetriaminecobalt(III) were removed by filtration on a Buckner funnel and washed with acetone until the wash was colourless. The wash and additional acetone was added to the mother liquor to give a final volume of 1 l. After standing two to three days a second crop of crystals was recovered. Found: Co, 22·00; C, 18·87; N, 15·45; Cl, 38·70. Calc. for [Co dien Cl_2]: Co, 21·94; C, 17·87; N, 15·64; Cl, 38·75%.

[Co dien $(NO_3)_2$]. When 5 g of trinitrodiethylenetriaminecobalt(III) was warmed with 5 ml of nitric acid, NO_2 was evolved leaving a deep violet solution. This solution was allowed to evaporate to a slurry at room temperature. By mixing 25 ml of acetone with the slurry and filtering on a Buckner, violet crystals of trinitrodiethylenetriaminecobalt(III) are left on the paper. These were washed with acetone and dried at 110°C. The yield was 5·2 g or 90 per cent. Found: Co, 17·00; C, 13·70. Calc. for [Co dien $(NO_3)_2$]: Co, 16·95; C, 13·80%.

Apparatus

All absorption spectra were obtained from a Beckman DK-2 spectrophotometer using matched 1·00 cm quartz cells. Distilled water was used as a reference.

DISCUSSION

Structure

To demonstrate the structure of diethylenetriamine complexes, three different lines of attack were employed. The first step was to attempt the resolution of the bis cobalt complex. Silver D-tartrate and silver D-camphor-β-sulphonate did not give crystalline salts. No optically active forms could be observed with the crystalline α-bromo-D-camphor-π-sulphonate salt.

The second step was to prepare a complex containing one molecule of diethylenetriamine and determine its structure. The inner nitrito complex was easily

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prepared directly from a simple salt. Its absorption peaks when compared to those of *cis* and *trans* trinitrotriamminecobalt(III) (Table 1) clearly showed it to be the *trans* form (Fig. 1a). This means that the amine molecule lies in a single plane as it did in the platinum compound previously described.

An attempt was then made to force the amine to occupy the corners of one octahedral face by the influence of the *trans* effect. The preparation of the trinitrotriamminecobalt(III) compound was repeated starting with sodium cobaltinitrite

TABLE 1

	mμ	log ε	mμ	log ε	mμ	log ε
[Co dien $(NO_2)_3$]	250	4·38	338	3·68	433	2·50
$[Co(NH_3)_2(NO_2)_3]$ *cis*	—	—	325	3·72	440	2·24
trans	251	4·26	340	3·65	434	2·52

and the *trans*- and the *cis*-trinitrotriamminecobalt(III). In the first two preparations, a product identical to the original was obtained. No product could be isolated from the preparation starting with *cis*-trinitrotriamminecobalt(III). This confirms the original identification of the *trans* form and emphasizes the strong tendency of the amine molecule to occupy the single planar position.

Properties of [M dien X_3] *compounds*

The remarkable stability and insolubility of trinitrodiethylenetriaminecobalt(III) created an interest in the properties of this and similar compounds. The molar solubility of [Co dien $(NO_2)_3$] in water was about 0·003 M. It was insoluble in common organic solvents. The complex reacted very slowly with acids at room temperature. The nitrite radical was decomposed, giving complex ions of varying composition containing hydroxyl or aquo groups or the anion of the acid used.

Careful studies of the reaction with hydrochloric acid revealed that the first reaction product was [Co dien $(NO_2)_2Cl$], a yellow compound. The water solubility of this compound was a little greater than the original trinitro complex. There was no apparent hydrolysis or ionization of the chloro group in neutral or acid solutions. The presence of silver ion in solution produced a slow but complete precipitation of the chloride. This chloride can be replaced by an amino group. When a bidentate amine is used a hydroscopic non-crystalline solid was obtained suggesting that the amine had acted as a monodentate. A comparison of the absorption bands (Table 2) of the chloro and amino derivative with similar known compounds indicates the *trans* position for the nitro groups in the trinitrotriammine complex. Presumably this is the position held in the dinitrochloro complex as well. This is not the expected configuration if the *trans* effect is operative. It does explain, however, the fact that the next reaction product with HCl is the trichloro complex.

The compound [Co dien Cl_3] crystallizes from strongly acid concentrated solutions as a deep brown solid with no lustre. It is readily soluble in water but hydrolyses to give a variety of ions depending on concentration and the concentration

of hydrochloric acid. A water solution of the compound is red, while its concentrated hydrochloric acid solution is green.

The only product isolated from the reaction of [Co dien $(NO_2)_3$] with nitric acid is [Co dien $(NO_3)_3$]. This is a deep violet solid which dissolves readily in water to give a red-violet solution. The absorption spectrum is distinctly different from that

TABLE 2

	mμ	log ε	mμ	log ε	mμ	log ε
[Co en_2 $(NO_2)_2$]$^+$ *cis*	240	4·22	325	3·62	433	2·34
trans	250	4·09	340	3·48	435	2·25
[Co dien (NH_3) $(NO_2)_2$]$^+$	250	4·25	346	3·49	447	2·27
[Co en_2 (NO_2)Cl]$^+$ *cis*	—	—	337	3·26	465	1·96
trans	245	4·19	340	3·14	446	1·91
[Co dien $(NO_2)_2$Cl]	245	4·20	336	3·57	449	2·32

of [Co dien $(H_2O)_3$]$^{3+}$ which was obtained by precipitating as silver chloride the chloride from a solution of [Co dien Cl_3]. A comparison of absorption bands is made in Table 3.

Two thiocyanto complexes, [Co dien $(SCN)_3$] and [Co dien $(SCN)_2OH$], can be made directly from simple cobalt salts. The former cannot be made in the presence of water since it is easily and rapidly hydrolysed to the hydroxo complex.

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TABLE 3

	mμ	log ε	mμ	log ε
[Co dien $(NO_2)_3$]	318	2·75	520	1·95
[Co dien $(H_2O)_3$]$^{3+}$	340	2·81	510	2·06
[Co$(NH_3)_3(H_2O)_3$]Cl_3 *cis*	376	—	578	—
trans	340	—	556	—

The compound [Co dien $(SCN)_2OH$] is easily made in water solution and appears to be quite stable. The solubility depends markedly on the pH of the solvent. Minimum solubility occurs at a pH 4–5 where a low of 0·01 M constitutes a saturated solution. The complex dissolves to give quite concentrated (1 M) solutions in sodium hydroxide solutions of pH 9–10. This is not what would be expected for a hydroxo complex. This complex showed absorption maxima at 308 mμ (log ε = 4·19), 330 mμ (log ε = 4·16) and 520 mμ (log ε = 2·39).

SUMMARY

The natural configuration for diethylenetriamine co-ordinated in an octahedron of cobalt is probably that in which the three co-ordinated positions lie in one plane. The occupation of the three corners of one octahedral face is unlikely if not impossible as demonstrated by the failure to resolve [Co $dien_2$]$^{3+}$. This supposition is strengthened

by the formation of *trans* form of [Co dien $(NO_2)_3$] using $[Co(NO_2)_6]^{3-}$ and the failure to prepare a compound of this type from *cis*$[Co(NH_3)_3(NO_2)_3]$.

The inner cobalt diethylenetriamine complexes present several strange chemical properties. The trinitro complex is very stable as is expected, but its first reaction product with hydrochloric acid removes only one nitro group leaving the remaining two in the *trans* relationship.

The inner complexes show considerably different tendencies to hydrolyse. No hydrolysis is observed for the trinitro complex; one thiocycanto group is removed from [Co dien $(SCN)_3$], and extensive hydrolysis of the trichloro complex is observed All of the compounds formed exhibited a strange passiveness to ammonia and propylenediamine.

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REMARKS ON THE TRINUCLEAR ACETATO COMPLEXES OF IRON(III), CHROMIUM(III) AND ALUMINIUM

K. STARKE*
Department of Chemistry, University of Kentucky, Lexington, Kentucky

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Abstract—The reaction between acetic anhydride and the hydrated nitrates of iron(III), chromium (III) and aluminium has been re-examined. Nitrates of unipositive acetato-hydroxo complexes are formed as intermediates whose composition is $[M_3(OCOCH_3)_7OH{\cdot}nH_2O]NO_3$ with n varying from 0 to 4. In the final stage of the reaction, an additional acetato group replaces the nitrate ion while the hydroxo group is carried into the end product. The reaction, therefore, is not useful for the preparation of the pure tri-acetates of the formula $M(OCOCH_3)_3$. The experiments provide evidence for unipositive trinuclear acetato complexes of aluminium whose existence has been obscured by their relatively low stability as compared to the complexes of iron and chromium.

THE acidimetric titration of metal acetates in glacial acetic acid by CASEY and STARKE[1] gave anomalous results in so far as it required only one-ninth of an equivalent of perchloric acid per equivalent of iron(III), chromium(III), and aluminium. At the end point, there must exist trinuclear complexes $[M_3X_8]^+$ with eight nonionizable groups. These could be all acetato or partly hydroxo groups as in the complex $[Fe_3(OCOCH_3)_6(OH)_2]^+$ found by TREADWELL and FISCH[2] in the titration of iron(III) chloride or nitrate with sodium acetate in aqueous solution. Numerous other unipositive trinuclear carboxylato complexes of iron(III) and chromium(III) have been isolated or studied in solution by WERNER, WEINLAND, KRAUSE, KÜNTZEL and others.

However, there is little support for the existence of analogous aluminium compounds. The complex nature of the acetate has been suspected by TREADWELL and ZÜRCHER[3] while titrating basic aluminium acetate with sodium hydroxide. Only SPACU and POPPER[4] have claimed clearly the existence of the ion $[Al_3(OCOCH_3)_6(OH)_2]^+$ in the system aluminium nitrate–sodium acetate. To add further evidence, the isolation of a trinuclear aluminium complex was attempted. The nitrate was chosen because corresponding iron and chromium compounds are known. Also, CASEY and STARKE[1] had heated the hydrated metal nitrates with acetic anhydride to produce metal acetate solutions in glacial acetic acid.

Originally, the reaction had been recommended by SPÄTH[5] for preparing the triacetates $Fe(OCOCH_3)_3$ and $Cr(OCOCH_3)_3$. Aluminium nitrate yielded the basic product $Al_2O(OCOCH_3)_4$. Later, the method was criticized by WEINLAND and REIHLEN,[6] who obtained hydroxo complexes of all three metals. In the present

* Present address: Institut für Kernchemie der Universität Marburg, Marburg (Lahn), Germany.

[1] A. T. CASEY and K. STARKE, *Analyt. Chem.* **31**, 1060 (1959).
[2] W. D. TREADWELL and W. FISCH, *Helv. Chim. Acta* **13**, 1209 (1930).
[3] W. D. TREADWELL and M. ZÜRCHER, *Helv. Chim. Acta* **15**, 980 (1932)
[4] G. SPACU and E. POPPER, *Kolloid Z.* **103**, 19 (1943).
[5] E. SPÄTH, *Monatsh.* **33**, 242 (1912).
[6] R. WEINLAND and H. REIHLEN, *Z. Anorg. Chem.* **82**, 426 (1913).

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investigation a variation was introduced by treating the metal nitrates at a low temperature in the presence of ethanol as reducing agent for the nitrate. The product then was heated with more acetic anhydride and the change in composition was determined.

EXPERIMENTAL

Materials

The chemicals were of analytical reagent purity, except for the solvents, which were of practical grade. 2,2-Dimethoxypropane (98 per cent) was used for its dehydrating effect.[17] Skellysolve A is a commercial mixture of pentanes (boiling range 30–38 C). Volume ratios are given for all solvent mixtures.

Analysis

Microanalyses were carried out by the Microanalytical Laboratory, Max Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany. If not stated otherwise, in parentheses following the percentage, the averages of two determinations are given.

Preparations

All products were dried in a vacuum desiccator over calcium chloride. In view of the debatable molecular weights of the compounds no percentage yields were calculated.

1. *Iron compounds.* (a) Iron(III) nitrate 9-hydrate (8·08 g, 0·02 mole) was warmed with 5 ml of absolute ethanol and allowed to react with 25 ml of acetic anhydride. The vigorous reaction was kept under control by cooling with ice water. After 17 hr red crystals had formed which were centrifuged and washed with glacial acetic acid and 2,2-dimethoxypropane-Skellysolve A (1 : 1). The amount obtained was 4·63 g; 0·11 g could be precipitated from the mother liquor by the solvent mixture mentioned. Both precipitates had practically the same composition and the average of all four determinations was taken. (Found: C, 23·99; H, 4·19; Fe, 24·01; N, 1·98. Calc. for $[Fe_3(OCOCH_3)_7OH{\cdot}2H_2O]NO_3$: C, 24·16; H, 3·77; Fe, 24·08; N, 2·01%).

(b) The compound (1·0 g) was recrystallized from 7 ml of warm glacial acetic acid and washed with acetic anhydride and 2,2-dimethoxypropane-Skellysolve A (1 : 1). The amount obtained was 0·77 g. (Found: C, 23·79; H, 3·94; Fe, 23·62; N, 1·86. Calc. for $[Fe_3(OCOCH_3)_7OH{\cdot}3H_2O]NO_3$: C, 23·55; H, 3·95; Fe, 23·47; N, 1·96%). The compound was soluble in water, methanol, ethanol, acetone, acetonitrile and warm glacial acetic acid.

(c) The filtrate from the recrystallization combined with the acetic anhydride washings deposited overnight 30 mg of a brick-red precipitate. (Found: C, 29·40; H, 3·91; Fe, 25·32 (1); N, 0·26 (1). Calc. for $Fe_3(OCOCH_3)_8OH$: C, 29·89; H, 3·80; Fe, 25·27; N, 0·00%). The compound was insoluble in organic solvents.

2. *Chromium compounds.* (a) Chromium nitrate 9-hydrate (8·00 g, 0·02 mole) was warmed with 5 ml of absolute ethanol and allowed to react with 25 ml of acetic anhydride with occasional cooling. After 17 hr green crystals had precipitated from the violet mother liquor. They were centrifuged and washed with glacial acetic acid and 2,2-dimethoxypropane-Skellysolve A (1 : 1). The amount obtained was 3·96 g. (Found: C, 24·89; H, 4·32; Cr, 22·10 (1); N, 1·77. Calc. for $[Cr_3(OCOCH_3)_7OH{\cdot}2H_2O]NO_3$: C, 24·57; H, 3·83; Cr, 22·80; N, 2·05%).

(b) The compound (1·0 g) was recrystallized from 9 ml of warm glacial acetic acid and washed with acetic anhydride and 2,2-dimethoxypropane–Skellysolve A (1 : 1). The amount obtained was 0·42 g. (Found: C, 24·97; H, 4·22; Cr, 22·29; N, 1·67. Calc. for $[Cr_3(OCOCH_3)_7OH{\cdot}2H_2O]NO_3$: C, 24·57; H, 3·83; Cr, 22·80; N, 2·05%). The compound was soluble in water, methanol, ethanol, acetone, acetonitrile and warm glacial acetic acid.

(c) The green filtrate from the recrystallization combined with the acetic anhydride washings was boiled on a hot plate with constant stirring. A green precipitate formed which contained practically all the chromium. (Found: C, 29·84; H, 4·14; Cr, 23·37; N, 0·05 (1). Calc. for $Cr_3(OCOCH_3)_8OH$: C, 30·42; H, 3·87; Cr, 23·95; N, 0·00%). The precipitate was insoluble in organic solvents.

(d) 2,2-Dimethoxypropane was added slowly to the violet filtrate obtained in (a) until crystallization started. The crystals were left to settle and precipitation was completed by adding Skellysolve

[17] K. Starke, *J. Inorg. Nucl. Chem.* **11**, 77 (1959).

A in small portions over a period of time. The amount of the pale violet powder obtained was 0·94 g. (Found: C, 26·67; H, 4·34; Cr, 24·35; N, 0·96. Calc. for $[Cr_6(OCOCH_3)_{14}(OH)_2 \cdot 2H_2O]NO_3$: C, 26·12; H, 3·84; Cr, 24·23; N, 1·09%). The precipitate was soluble in water, methanol, ethanol, acetonitrile and glacial acetic acid.

The compound (0·5 g) was dissolved in 2 ml of glacial acetic acid. Overnight only a few milligrams of crystals separated out which were not sufficient for complete analysis.

(e) The filtrate from the attempt to recrystallize the violet compound was heated with acetic anhydride on the hot plate with constant stirring. It turned green and finally green crystals formed containing practically all the chromium. (Found: C, 29·75; H, 4·18; Cr, 23·39; N, 0·07 (1). Calc. for $Cr_3(OCOCH_3)_8OH$: C, 30·42; H, 3·87; Cr, 23·95; N, 0·00%). The precipitate was insoluble in organic solvents.

3. *Aluminium compounds.* (a) Aluminium nitrate 9-hydrate (7·50 g, 0·02 mole) was warmed with 5 ml of absolute ethanol and allowed to react with 25 ml of acetic anhydride with occasional cooling. After 17 hr, dissolved nitrous oxides were removed by adding absolute ethanol dropwise and warming slightly. 2,2-Dimethoxypropane-Skellysolve A (1 : 1) was added slowly to the filtered solution until crystallization started. Precipitation was completed by adding Skellysolve A in small portions over a period of time. The crystals were left to settle, centrifuged, washed with the solvent mixture mentioned and finally with Skellysolve A. The amount obtained was 4·04 g. The product was not perfectly white and was not analysed before recrystallization.

(b) The product (1·0 g) was recrystallized from 5 ml of warm glacial acetic acid. Crystals formed overnight which were centrifuged, washed with acetic anhydride and finally with 2,2-dimethoxypropane-Skellysolve A (1 : 1). The amount obtained was 0·48 g. (Found; C, 27·95; H, 4·79; Al, 14·76; N, 1·54. Calc. for $[Al_6(OCOCH_3)_{13}(OH)_4 \cdot 2H_2O]NO_3$: C, 28·51; H, 4·32; Al, 14·78; N, 1·28%). The compound was completely soluble in methanol, ethanol, acetonitrile and glacial acetic acid; it was hydrolysed by water.

(c) The filtrate from the recrystallization combined with the acetic anhydride washings was boiled on a hot plate with constant stirring. A white precipitate formed slowly. It was washed with acetic anhydride and finally with 2,2-dimethoxypropane-Skellysolve A (1 : 1). The amount obtained was 0·16 g. (Found: C, 32·90; H, 4·53; Al, 14·91; N, 0·05. Calc. for $Al_6(OCOCH_3)_{15}(OH)_3$: C, 32·80; H, 4·40; Al, 14·74; N, 0·00%). The precipitate was insoluble in organic solvents.

The following products were obtained by variations of methods (a) and (b).

(b′) Aluminium nitrate 9-hydrate (7·50 g, 0·02 mole) was warmed with 4 ml of absolute ethanol and allowed to react with 26 ml of acetic anhydride. At the end of the reaction, 2 ml of absolute ethanol was added. The solution was diluted with 40 ml of 2,2-dimethoxypropane, treated with charcoal and filtered into a centrifuge glass. 2,2-Dimethoxypropane–Skellysolve A (1 : 1) was added slowly until crystallization was complete. The crystals were allowed to settle, centrifuged and washed with the solvent mixture mentioned. Centrifugation and washing was repeated and exposure of the precipitate to the atmosphere kept at a minimum until the hygroscopic reaction product acetic acid had been removed. The amount obtained was 3·2 g.

The crystals were dissolved in 100 ml of acetonitrile–2,2-dimethoxypropane–glacial acetic acid (89 : 10 : 1) at 50°C. The solution was filtered and 100 ml of warm 2,2-dimethoxypropane–Skellysolve A (1 : 1) was added. Crystallization was completed with more of the solvent mixture and finally with Skellysolve A. The crystals were left to settle for several days, separated by suction and washed with Skellysolve A. The amount obtained was 2·57 g. (Found: C, 29·06; H, 4·84; Al, 14·00; N, 2·50 (1). Calc. for $[Al_3(OCOCH_3)_7OH]NO_3$: C, 29·33; H, 3·87; Al, 14·12; N, 2·44%).

(b″) The mother liquors of the preceding and similar preparations were set aside. In one case, after several weeks, large plates crystallized out, which were collected and analysed. (Found: C, 29·71; H, 5·11; Al, 13·63; N, 2·38. Calc. for $[Al_3(OCOCH_3)_7OH]NO_3$: C, 29·33; H, 3·87; Al, 14·12; N, 2·44%). Unlike (b) and (b′), this sample gave a clear solution in acetonitrile after one year in a desiccator. Attempts to work out a reproducible method of preparation of these large crystals have failed so far.

DISCUSSION

In Table 1, the acetate and nitrate contents in gramme ions per three gramme ions of metal, are compared in the complexes of iron(III), chromium(III) and aluminium. They were calculated from the percentages of carbon, nitrogen and metal found. The

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letters in parentheses refer to the paragraphs in the experimental part. Data and references for comparable compounds in the literature are added. The values were calculated from the percentages of acetate, acetyl, nitrate and metal reported. The various moles of water which agree best with the analytical data are listed.

The test for nitrate with diphenylamine was positive in all compounds, though the percentage in the final products was negligible. In general, the nitrate/metal

TABLE 1.—GRAMME IONS OF ACETATE AND OF NITRATE PER THREE GRAMME IONS OF METAL IN ACETATO COMPLEXES OF IRON(III), CHROMIUM(III) AND ALUMINIUM

		Intermediate products			Final products	
		Water of hydration	Acetate	Nitrate	Acetate	Acetate gained
Fe	Present investigation	3	7·0[b]	0·9[b]	8·1[c]	1·1
		2	7·0[e]	1·0[e]		
	WEINLAND and co-workers	4	7·0[g]	1·0[g]	8·3[d]	
		3	7·0[g]	1·0[g]		
	SPÄTH				8·9[a]	
Cr	Present investigation	2	7·3[b]	0·8[b]	8·3[c]	1·0
		2	7·3[e]	0·9[e]		
	WEINLAND and co-workers	2·5	6·7[g]	1·0[g]	8·1[d]	
	SPÄTH				9·1[a]	
Al	Present investigation	1	6·4[b]	0·6[b]	7·4[c]	1·0
		0	7·0[b,c]	1·0[b,c]		
		0	7·3[b,e]	1·0[b,e]		
	SPÄTH				6·3[a]	

ratios point to a unipositive, trinuclear complex formed as an intermediate. WEINLAND and DINKELACKER[9] have mentioned briefly the production of an intermediate chromium complex by reaction with acetic anhydride, However, SPÄTH[5] and later WEINLAND and REIHLEN[6] passed this stage of the reaction by heating the mixture from the beginning. The acetate/metal ratios of the intermediate products range from 6·4 : 3 to 7·3 : 3 and do not reach 8 : 3. The products must contain hydroxyl in addition to acetate and nitrate.

The stability of the compounds is low, in particular that of the aluminium complex. Also, their molecular weights are high and uncertain because of the varying amounts of water of hydration retained after drying. All formulas derived from analytical data only must be somewhat speculative. Indeed, WEINLAND and co-workers postulated

[8] R. WEINLAND, K. KESSLER and A. BAYERL, *Z. Anorg. Chem.* **132**, 209 (1924).
[9] R. WEINLAND and P. DINKELACKER, *Ber. Dtsch. Chem. Ges.* **42**, 2997 (1909).

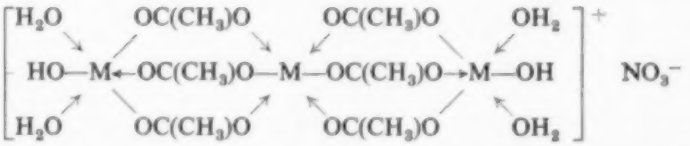
formulas for the iron and chromium compounds that differ from each other. They excluded from the complex not only the nitrate but also one acetate and all or part of the crystal water. Regarding all acetato groups as part of the complex, one can express the compounds obtained by WEINLAND by the general formula $[M_3(OCOCH_3)_7OH{\cdot}nH_2O]NO_3$ ($n = 0$–4). This applies also to the products of the present investigation, except the recrystallized aluminium compound (b). It has much lower acetate and nitrate/metal ratios than precipitates (b′) and (b″) which were prepared and recrystallized with special care to avoid hydrolysis.

Though violet acetato chromium complexes have been observed before,[10,11] neither SPÄTH nor WEINLAND and REIHLEN mention the production of a violet compound in the reaction of chromium nitrate 9-hydrate with acetic anhydride. The product (d) obtained in the present investigation dissolves easily in acetic acid, in which it turns green on warming with acetic anhydride. This might be expected of a mononuclear precursor of the green trinuclear complex; indeed both violet and green complexes yield the same insoluble end product, (c) and (e). On the other hand, the composition of the violet product (d) points to a hexanuclear complex. The interesting colour change should facilitate further investigations that appear necessary.

The reaction with acetic anhydride was most vigorous with iron(III) nitrate and slowest with aluminium nitrate. The same order could be observed in the final stage of the reaction with an excess of acetic anhydride. The iron precipitated completely overnight. The solution was not heated and apparently a small amount of nitrate was trapped in the crystals. The precipitation of aluminium, like that of chromium, required heat, but, unlike that of iron and chromium, was incomplete even after a long period of time.

The nitrate content in all three precipitates was negligible. The increase in acetate ions shows that they replaced the nitrate ions. In agreement with the results of WEINLAND and REIHLEN, the ratio 9 : 3 required for the triacetate could not be obtained. Again, the aluminium precipitate (c) has the lowest acetate/metal ratio. The product formulated by SPÄTH[5] as $Al_2O(OCOCH_3)_4$ should not be regarded as a definite compound. The author himself emphasized that it did not dissolve completely in water.

The variations in composition, as shown by Table 1, must have been caused by various amounts of water incompletely removed during the preparation or attracted from the atmosphere afterwards. Apparently, in all cases the concentration of water was low enough to allow the formation of a trinuclear complex with six acetato bridges.[12,13] Initially, hydrated metal ions reacted and it is plausible that at one point the well known hexaacetato-dihydroxo-tetraaquo complex was formed:



According to the analytical data, the reaction passed through this stage. However, it failed to produce a complex with all water molecules and hydroxyl groups removed

[10] R. WEINLAND and E. BÜTTNER, *Z. Anorg. Chem.* **75**, 293 (1912).
[11] A. KÜNTZEL, H. ERDMANN and H. SPAHRKÄS, *Das Leder* **4**, 73 (1953).
[12] R. WEINLAND, *Ber. Dtsch. Chem. Ges.* **41**, 3236 (1908).
[13] A. WERNER, *Ber. Dtsch. Chem. Ges.* **41**, 3447 (1908).

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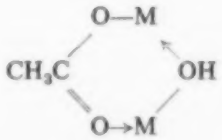
by reaction with acetic anhydride and acetic acid, that is, an octaacetato complex solvated by acetic acid molecules. Even if formed first, an octaacetato complex could easily undergo hydration and hydrolysis. The solvent, acetic acid, is quite hygroscopic[14] and the two non-bridging acetato groups would be relatively loosely bound.

The intermediate reaction products are crystalline; however, the analytical data cannot definitely establish whether they are nitrates of heptaacetato complexes or mixtures, isomorphic or not, of hexa- and octaacetato complexes. There is also the possibility of a water molecule and a hydroxyl ion taking the place of an acetate ion in the lattice. In this case, products with various acetate/metal ratios could crystallize out depending on the equilibrium reached between the two complex ions mentioned.

The hypothetical nitrate of an octaacetato complex is the intermediate which could be expected to yield normal metal triacetates in the final stage of the reaction. When the last nitrate ion is replaced, an acetate of an octaacetato complex is not likely to be stable. The strongly basic acetate ion should accept a proton from the solvated complex rendering it uncharged. Losing acetic acid, the trinuclear units could form polynuclear complexes of high molecular weight with continuous acetato bridges.

A polymerization process is indicated by the abrupt decrease in solubility as the final products are formed. It is accompanied by a gain of one gramme ion of acetate, regardless of the number of acetato groups in the intermediate complex. It appears that the polymerization begins before the complex is completely co-ordinated with acetato groups. This would create mixed acetato-hydroxo bridges forming particularly stable six membered rings.[11,15]



Metal triacetates should result under absolutely anhydrous conditions. Indeed, iron(III) triacetate crystallized out when the precautions were taken to concentrate its acetic acid solution slowly in a vacuum desiccator.[16] Also, aluminium triacetate was formed in the reactions of aluminium[17] and of aluminium chloride[18] with acetic acid and acetic anhydride, and of aluminium isopropoxide[19,20] with acetic anhydride.

It is interesting to note the behaviour of cerium(III) and lanthanum, whose nitrates have also been treated with acetic anhydride.[21,22] The intermediate products[21] had nitrate/metal ratios of 2 : 1 as compared to 1 : 3 for iron, chromium and aluminium. The intermediates have been reported to yield normal triacetates after further heating with acetic anhydride. However, more recent work on lanthanum

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[19] R. C. MEHROTRA and K. C. PANDE, *J. Inorg. Nucl. Chem.* **2**, 60 (1956).
[20] K. C. PANDE and R. C. MEHROTRA, *Z. Anorg. Chem.* **286**, 291 (1956).
[21] A. KOTOWSKI and H. LEHL, *Z. Anorg. Chem.* **199**, 183 (1931).
[22] S. PANDA and D. PATNAIK, *J. Indian Chem. Soc.* **33**, 877 (1956).

acetates[23] makes it probable that these final products are also polynuclear, or at least dinuclear, basic acetates.

CONCLUSION

The re-examination of the reaction between acetic anhydride and the hydrated nitrates of iron(III), chromium(III) and aluminium shows that all three metals form unipositive trinuclear acetato complexes as intermediates. They have the composition $[M_3(OCOCH_3)_7OH]NO_3$ which, for iron and chromium, has been reported before by WEINLAND and co-workers. The results agree with the claim of SPACU and POPPER that trinuclear acetato aluminium complexes exist in solution in analogy to iron and chromium, and also with the completely analogous behaviour observed when the three metals were titrated in glacial acetic acid by CASEY and STARKE. The aluminium ion forms the least stable complex, which can be expected in view of its inert gas electronic configuration.

If the acetato and hydroxo groups are equally nonionizable, the reaction may remain useful for the dissolution and titration of these metals in glacial acetic acid in spite of the variable composition of the trinuclear complexes which apparently depends on traces of water present.

Unlike the nitrate ions, the hydroxo groups are not replaced by acetate ions when heated with excess acetic anhydride. In agreement with WEINLAND and REIHLEN one must conclude that the reaction is not useful for preparing iron(III) and chromium(III) triacetates as claimed by SPÄTH.

Further investigation of these theoretically and practically important carboxylato complexes should include X-ray studies to establish definitely their structure.

Acknowledgements—The author is indebted to Prof. L. F. AUDRIETH for a discussion of the results before publication. The financial support by an Arts and Sciences Faculty Research Grant of the University of Kentucky is gratefully acknowledged. Thanks are also due to the Dow Chemical Company, Midland, Michigan, for a generous supply of 2,2-dimethoxypropane.

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SOME ELECTROMETRIC MEASUREMENTS OF HETEROPOLY ION FORMATION IN AQUEOUS SYSTEMS

P. CANNON*
University of Exeter

(*Received* 7 *January* 1959; *in revised form* 14 *July* 1959)

Abstract—Use is made of the deviation from linearity of the electrometric properties of mixed solutions of e.g. sodium molybdate and phosphate on titration with acid for determining the extent of combination between the components. The deviation from the titres required by the principle of isohydry to bring the solutions to pH 3·45 is proposed as a preferred measure of such combination. The results confirm existing knowledge concerning the formation and stability of phospho- and arseno-molybdates and tungstates.

THE formation of heteropoly phospho- and arseno-molybdates and tungstates in aqueous solution has been studied conductometrically and electrometrically,[1–8] colorimetrically,[9] polarographically,[10] by diffusion studies[11] and an attempt has been made to follow it refractometrically,[12] yet we still have no exact knowledge of the way in which these bulky anions are formed. On the other hand, there is a relatively exact body of information on the structures of these materials in the solid state, and in the case of the isopoly acids, a considerable amount of inference from the solid to the dissolved state is being used in the elucidation of e.g. titration data. The fact that some heteropoly acids are more dissociated than the related isopoly species[8] offers a different approach to the titrimetric study than has hitherto been employed: namely, to titrate the simplest alkali salts of the component acids with a very strong acid,[13] both separately and in mixed solution, and by comparison of the results over a wide range of molar ratios of, e.g., P : Mo, to find which heteropoly anions are formed in solution, and to gain at least a qualitative knowledge of their stability and acid strength. This has been done in the present work, in the phosphate–molybdate and tungstate and arseno–molybdate and tungstate systems. The principal advantages of this technique are the convenience of the reagents (for purity) and the comparative absence of confusion due to hydrolytic instability, which complicates alkalimetric studies on the prepared heteropoly species.

* Present address: General Electric Research Laboratory, Schenectady, New York.

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[11] G. JANDER and K. F. JAHR, *Koll. Beihefte* **41**, 297 (1934).
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[13] H. T. S. BRITTON and P. JACKSON, *J. Chem. Soc.* 1055, (1934).

EXPERIMENTAL

Chemicals and procedure

Solutions were prepared from AR grade materials (Hopkin and Williams Ltd.), the concentrations of master solutions being checked by gravimetric analysis for Mo, W, P or As. Care was taken that the concentrations of Na_2MoO_4 and Na_2WO_4 were such that the reaction between them and hydrochloric acid might best be represented as

$$4Na_2XO_4 + 6HCl \rightarrow Na_2O(XO_3)_4 + 6NaCl + 3H_2O$$

where X presents Mo or W, respectively. The molybdate (or tungstate) solutions were mixed with the phosphate (or arsenate) solutions so that the concentration of molybdate (or tungstate) was

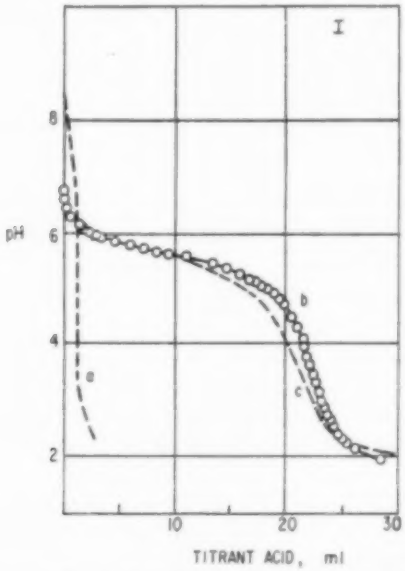

FIG. 1.—Glass electrode titrations with 1·000 N HCl of (a) 200 ml 0·0055 M Na_2HPO_4 (b) 200 ml 0·0055 M Na_2HPO_4, 200 ml 0·066 M Na_2MoO_4: composite curve obtained by adding abscissae at a given pH. (c) observed titration curve of 200 ml of a mixed solution 0·0055 M Na_2HPO_4 + 0·066 M Na_2MoO_4.

constant throughout a given set, yet any desired ratio of molybdate (or tungstate) to phosphate (or arsenate) might be obtained.

The progressive addition of hydrochloric acid to these mixed solutions was followed conductometrically and by means of the glass electrode. The observed pH curves were compared with calculated curves (from the principle of isohydry): the pH titration curves with hydrochloric acid of the component solutions of the mixtures were determined separately, the titres of acid required to give a particular pH were added and the combined titre plotted against the pH. In this manner a composite curve was obtained (Fig. 1). The extent of the divergence between the observed and composite curves was regarded as a measure of the extent of combination between the solutes. These divergences are shown on Figs. 2–5 plotted vs. the ratio of phosphate (or arsenate) to molybdate (or tungstate), together with lines indicating the amounts required by simple replacement reactions. The divergences were measured at pH 3·45, which is the pH which would be expected were one drop of unreacted titrant acid present in the solution: this value consequently represents the "end-point" of the titration.

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Apparatus

The apparatus was the same and was calibrated in the same way as described in a previous investigation.[14] Steamed out, new Pyrex ware was used and the titrations were done under nitrogen. Precautions against excessive dilution of the test solutions were also employed.

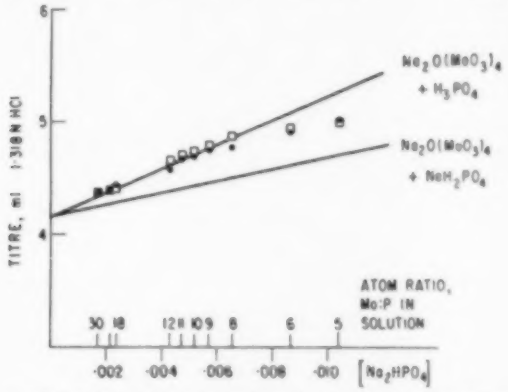

FIG. 2.—Titres of 1·318 M HCl required to bring 70 ml of solution 0·05214 M w.r.t. $Na_2MoO_4 + x$ M Na_2HPO_4 to pH 3·45 (●) and to the mathematical inflexion in the titration curve (□), plotted vs. molarity of Na_2HPO_4. Solid lines indicate titres calculated for indicated products of reaction.

Rates of reaction

Equilibrium was reached rapidly in the molybdate–phosphate system, only about 5 min being necessary and then only in the regions about pH 4. In the case of the molybdate–arsenate systems, individual points took some 15 min to equilibrate. Equilibrium in the phosphate- and arsenate-tungstate systems was attained more rapidly than in the case of regular tungstate systems. In general a matter of 10 min was required for steady values of pH and K to be obtained.

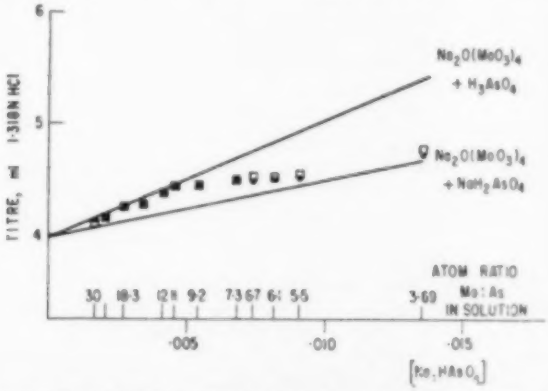

FIG. 3.—Titres of 1·318 M HCl required to bring 70 ml of solution 0·0495 M w.r.t. Na_2MoO_4 + x M Na_2HAsO_4 to pH 3·45 (●) and to the mathematical inflexion in the titration curve (□), plotted vs. molarity of Na_2HAsO_4. Solid lines indicate titres calculated for indicated products of reaction.

Colour changes and precipitation during titration

Those solutions containing molybdate and phosphate in molar ratios less than nine became bright yellow at about pH 5–4, whereas those in which this ratio was greater possessed a much fainter

[14] P. CANNON, *J. Inorg. Nucl. Chem.* **9**, 252 (1959).

colour on acidification. No precipitation was observed during the course of the titrations, or during a period of one week subsequent to the titration.

The presence of small amounts of arsenate in molybdate solutions caused the production of a faint yellow colour, when the titration was near the end-point. The intensity of this colour increased

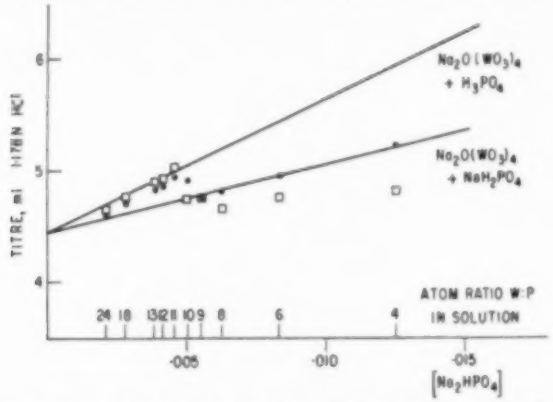

FIG. 4.—Titres of 1·178 M HCl required to bring 70 ml of solution 0·05000 M w.r.t. Na_2WO_4 + x M Na_2HPO_4 to pH 3·45 (●) and to the mathematical inflexion in the titration curve (□), plotted vs. molarity of Na_2HPO_4. Solid lines indicate titres calculated for indicated products of reaction.

up to the molar ratio arsenate : molybdate 1 : 12, but thereafter decreased until the solutions possessed only a very faint lime colour, when the ratio arsenate : molybdate was greater than 1 : 9. A spectrophotometric study was not undertaken, because of the difficulties attached to the interpretation of the results: the spectra possess no peaks. No precipitation was seen in this system.

No colour changes were seen in the tungstate systems.

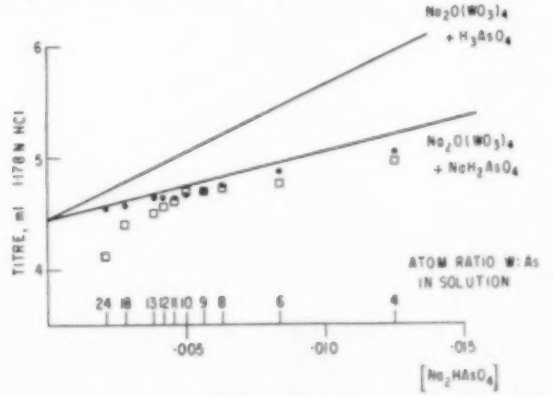

FIG. 5.—Titres of 1·178 M HCl required to bring 70 ml of solution 0·05000 M w.r.t. Na_2WO_4 + x M Na_2HAsO_4 to pH 3·45 (●) and to the mathematical inflexion in the titration curve (□), plotted vs. molarity of Na_2HAsO_4. Solid lines indicate titres calculated for indicated products of reaction.

RESULTS

(a) *Molybdate–phosphate and molybdate–arsenate systems*

The observed pH titration curves consist of two main sections; the first a sharp decrease in pH from 8 to about 6: the second a buffer range from pH 6 to pH 5, and a terminal inflexion in the vicinity of pH 3.

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The section corresponds with the reaction

$$Na_2HYO_4 + HCl \rightarrow NaH_2YO_4 + NaCl,$$

where Y is P or As, since the values of pH set up in these sections (which are regarded as extending to the amount of acid required for the above reaction), correspond very closely with the values calculated from the published values of pKa_2[15] for phosphoric and arsenic acids, during the addition of as much as 60 per cent of the total quantity of hydrochloric acid. The titres of acid required to bring the curves to their final inflexions, and to a pH of 3·45, are shown on Figs. 2 and 3. There is a substantial excess of hydrochloric acid, over that required to form sodium tetramolybdate and monosodium phosphate, required to bring each solution to pH 3·45: for those solutions in which the P : Mo ratio lay between 1 : 30 and 1 : 9, the amounts of excess acid are very similar to those required to form phosphoric acid. At values of the P : Mo ratio higher than 1 : 9, the divergences are smaller. The conductometric data in the last stages of acidification also correspond closely to the addition of hydrochloric acid to a system containing tetramolybdate and phosphoric acid, yet this phosphoric acid must be in combination with the molybdate, since the pH values are higher than those which would be anticipated were free phosphoric acid present in solution. It is also evident that there is no tendency for this combination to occur at P : Mo ratios greater than 1 : 9, since in these cases the titre to pH 3·45 remains essentially constant, replacement of the additional phosphate taking place in the normal manner at a lower pH.

The pH values at the positions corresponding with the composition of the solutes sodium tetramolybdate: monosodium phosphate increase from pH 3·80 (phosphate : molybdate 1 : 30) to pH 4·45 (phosphate : molybdate 1 : 9), and thereafter are constant. With no interaction occurring, these values would be constant throughout.

As with the conductivity data, the pH values set up below 3·45 correspond most nearly with those calculated for the addition of hydrochloric acid to a system containing tetramolybdate and phosphoric acid.

Attempts to follow the interaction directly via the interaction of supersaturated solutions of molybdic oxide dihydrate and phosphoric acid ([MoO_3] lying between 0·1296 M and 0·01296 M) gave only small changes in pH and conductivity. The MoO_3 : H_3PO_4 ratios at which these changes were maximized were dependent on solution concentration, which may account for the discrepancies between the earlier studies of ROSENHEIM and JAENICKE, and MIOLATI[2,3]. Studies involving the measurement of the solubility of molybdic oxide hydrate ($MoO_3 \cdot H_2O$) in various acids by the present author[16] indicate that $MoO_3 \cdot H_2O$ is less soluble in concentrated phosphoric acid than dilute.

The molybdate–arsenate system exhibits the behaviour described above, with the following differences. In solutions containing arsenate and molybdate up to the ratio 1 : 12, all the arsenate present in solution combines with the sodium tetramolybdate present on the addition of hydrochloric acid to form a complex arseno 12 : molybdate. With solutions containing a higher ratio of arsenate : molybdate, not even this small quantity of arsenate appears to combine with the molybdate, at least, not in the manner presented above.

[15] H. T. S. BRITTON and P. JACKSON, *J. Chem. Soc.* 1049 (1934).
[16] P. CANNON, *J. Inorg. Nucl. Chem.* **11**, 124 (1959).

A comparison of the observed curves with those calculated from the principle of isohydry shows the delaying effect only qualitatively in this case. Further, the values of pH set up in solution when the composition of the solution corresponded with that of a mixture of sodium tetramolybdate and monosodium arsenate did not vary as much as did those found in the similar case with sodium phosphate and sodium molybdate. The positions of the conductometric breaks correspond less closely with the positions of the inflexions in the glass electrode titration curves than did those observed in the molybdate–phosphate system. The breaks do, however, correspond more closely with the titres required for the formation of sodium tetramolybdate and arsenic acid than did the inflexions, especially in those solutions in which the arsenate : molybdate ratio was less than 1 : 9. The curves themselves show that the final steep rise in conductivity is delayed in those solutions containing arsenate and molybdate in the molar ratios up to 1 : 12, until sufficient acid has been added to form sodium tetramolybdate and arsenic acid. This latter must have combined with the tetramolybdate, since the increase in conductivity which might be expected due to its presence is not observed.

(b) *Tungstate–phosphate system*

The glass electrode curves are inflected twice (in a manner similar to the behaviour of tungstate alone) for those solutions in which the phosphate : tungstate ratio was less than 1 : 12, but only once with those solutions in which the phosphate : tungstate ratio was greater than this value. The buffer range of all these curves is higher than in the case of solutions containing sodium molybdate, and consequently, the first portion of the curves, which would be expected to show values of pH due to the replacement of monosodium phosphate from disodium phosphate, is not visible.

The titres to pH 3·45 and those required to produce the inflexion for those solutions with a P : W ratio less than 1 : 11, are in agreement with those calculated for the production of sodium tetratungstate and phosphoric acid, but above this ratio, they tend to be in agreement with those calculated for the formation of sodium tetratungstate and monosodium phosphate (Fig. 4). The observed conductometric titres are in close agreement with the titres required to bring the solutions to pH 3·45. The observed pH values below 3·45 once more agree with the addition of hydrochloric acid to a solution in which no further reaction occurs.

The production of a complex solute in this case appears to depend in part on the length of time allowed to elapse between the acidification of the tungstate solution and the addition of phosphoric acid. Thus it was found that freshly prepared tungstic oxide would dissolve only in phosphoric acid solutions, aged tungstic oxide would not dissolve in 8 M hydrochloric acid, 16 M phosphoric acid or in 10 M nitric acid. It was found that if sufficient phosphoric acid was added to the fresh tungstic oxide in the molar ratio 1 : 12, a clear solution was obtained after shaking for thirty minutes. With smaller ratios of phosphoric acid : tungstic oxide, much of the latter remained; with higher ratios, clear solutions were obtained very readily but they later deposited tungstic oxide. However, no precipitation was observed throughout the course of the titrations described above. It appeared very likely that the effect of ageing the tungstic oxide was physical rather than chemical, the important fact

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being that tungstic oxide was precipitated from those solutions in which more phosphoric acid was present than was required for the formation of a phospho-12-tungstic acid. This supports the observations made during the titrations, that the extent of combination actually tends to decrease at ratios of phosphate : tungstate much greater than 1 : 12.

(c) *Tungstate–arsenate systems*

The potentiometric titration curves of these solutions with hydrochloric acid are all similar to one another. They start with a buffered portion, from pH 7 to pH 5·5, and then terminate, with a single inflexion, in the vicinity of pH 4. These inflexions were difficult to locate, and the titres that were required to produce them are shown, together with the titres required to bring the solutions to pH 3·45, on Fig. 5. The titres required to produce the breaks in the conductometric curves correspond almost exactly to those calculated for the formation of sodium tetratungstate and monosodium arsenate, thus suggesting that the acidification of solutions containing arsenate and tungstate in any of the ratios studied does not result in the formation of a complex solute of the type that was found in the case of the phosphomolybdate and phosphotungstate. The presence of arsenate does however cause a modification of the titration curve, compared with that calculated from the principle of isohydry, in the pH range 7–5.

DISCUSSION

The results of the present work stand in support of existing knowledge concerning the strength of the various heteropoly anions involved, specifically showing the greater ease with which phospho-12-molybdates may be formed by comparison with the arseno-12-molybdates. In the case of the tungstate systems, the situation is more complex because of the peculiar influence of time. Thus SOBOLEEFF[17] stated that the reaction between solutions of phosphoric acid and metatungstic acid does not occur, and MALAPRADE[18] noted the reaction to be very slow. However, it is known from the directions of SCHIEBLER[19] for the preparation of the complex that the above acidification produces the complex quite readily, and hence it appears that some difficulties may arise with the age of the acidified tungstate solutions, since metatungstic acid itself is only obtained from such solutions after some time. Similarly, solid tungstic oxide, once separated from solution, has been reported not to be soluble in any acid save very concentrated hydrochloric acid, in marked contrast with molybdic acid, which even after being dried at 130°C, dissolves readily in quite dilute hydrochloric acid.

KEHRMANN and RUTTIMANN,[20] and ROSENHEIM and JAENICKE[1] have reported that arseno-12-tungstic acid cannot be obtained in the free state. The only arsenotungstic acid the existence of which has been confirmed, namely $As_2O_5 \cdot 18WO_3 \cdot 42H_2O$ is not obtained by the simple acidification mentioned above[2,19,21] and it seems likely that under normal acidification conditions there is not interaction between the components to give a complex arsenotungstate.

[17] M. SOBOLEEFF, *Z. Anorg. Chem.* **12**, 25 (1896).
[18] L. MALAPRADE, *Ann. Chim.* [10] **11**, 159; 195 (1929).
[19] C. SCHIEBLER, *Ber. Dtsch. Chem. Ges.* **5**, 801 (1872).
[20] F. KEHRMANN and E. RUTTIMANN, *Z. Anorg. Chem.* **22**, 285 (1899).
[21] F. KEHRMANN, *Liebigs Ann.* **245**, 53 (1888).

It seems that the use of the titre to pH 3·5 could well be extended for work in systems of this kind. It is quite evident from the titration curves that reaction to give the heteropoly species occurs immediately the "tetra" or "meta" molybdate ion forms, but not before: with the tungstate solutions it is necessary to give the first formed "para" tungstate time to go over to the "meta" form before any unusual effects are seen. The influence of time is in this case confused by the effect of hydrogen ion concentration on the para-meta equilibrium.

Acknowledgements—I am grateful to the Senate and Council of the University of Exeter, the Ministry of Education of H.M. Government and the Foundation Governors of King Edward VI School, Totnes, for the award of scholarships.

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THE REACTION OF ALKALI TUNGSTATE SOLUTIONS WITH HYDROCHLORIC ACID

P. CANNON
University of Exeter*

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Abstract—Careful electrometric and conductometric data are presented which make possible a direct comparison of the results of earlier workers in different concentration ranges. In this way, previous small discrepancies are resolved and the previously accepted notion of an unstable "para" ion and a strong "meta" ion is further confirmed. Absorptiometric studies offer an independent corroboration of the above and probably a more sensitive tool for the investigation of such systems.

THE polymerization of tungstate anions in aqueous solution by the addition of strong acids has been frequently studied, but divergent interpretations have been placed upon the results obtained. Studies involving electrometric and conductometric titration have been made by (among others) BRITTON and GERMAN,[1] DUMANSKI *et al.*,[2] ROSENHEIM and WOLF,[3] BRINTZINGER and RATANARAT,[4] JANDER *et al.*,[5,6] and SOUCHAY *et al.*,[7] all using slightly different techniques under slightly different system conditions. As a consequence, their results vary in a detailed manner, but are all in general agreement with the results obtained by JANDER *et al.*, using the diffusion measurement technique, which are indicative of a substantial polymerization occurring at molar ratios of acid : tungstate, [HX] : [WO_4''], greater than 1·5. Some more weakly defined interactions were found by some of these workers to take place at ratios rather lower than the above, particularly at the ratio [HX] : [WO_4''] ca. 1·14 (the two ratios cited correspond with the so-called "meta" and "para"-tungstates, respectively).

Relatively minor differences in the titration data yield rather substantial differences in the polytungstate empirical formula; consequently, much of the earlier discussion on this subject appears possibly to have risen from the use of different techniques and conditions by the various workers. One of the purposes of the present note is to report titration experiments done with more sensitive equipment than was available to some of the earlier workers, avoiding the use of techniques which interfere with the studied system (e.g. the use of the hydrogen electrode[3]). Some interesting confirmatory data from absorption photometry is also reported.

EXPERIMENTAL

Conductometric and glass electrode titrations, and absorption spectra, were determined using the same techniques that have been described elsewhere.[8]

The glass electrode titration curves all show two inflexions at [HX] : [Na_2WO_4] equal to 1·14 and 1·50. The addition of hydrochloric acid was accompanied by visible changes in the appearance of the

* Present address: General Electric Research Laboratory, Schenectady, New York.

[1] H. T. S. BRITTON and W. L. GERMAN, *J. Chem. Soc.* 1249 (1931).
[2] A. V. DUMANSKI, A. P. BUNTIN, S. Y. DIJATSCHOWSKI and A. C. KNIGA, *Kolloid Z.* **38**, 208 (1926).
[3] A. ROSENHEIM and A. WOLFF, *Z. Anorg. Chem.* **193**, 447 (1930).
[4] H. BRINTZINGER and C. RATANARAT, *Z. Anorg. Chem.* **224**, 97 (1935).
[5] G. JANDER and W. HEUKESHOVEN, *Z. Anorg. Chem.* **187**, 60 (1930).
[6] G. JANDER and V. KRUERKE, *Z. Anorg. Chem.* **263**, 244 (1951).
[7] P. SOUCHAY *et al.*, *Ann. Chim.* [11], **19**, 102 (1944); [11], **20**, 73 (1945); [12], **2**, 203 (1947).
[8] P. CANNON, *J. Inorg. Nucl. Chem.* **9**, 252 (1959).

two more concentrated solutions. Initially, the local excess of hydrochloric acid, caused by the drops of acid entering the solution, caused the appearance of a white solid, which redissolved in a short time. This behaviour continued until 1·14 equivalents of acid had been added, when the pH of the solution began to drop rapidly, and the local precipitation was not observed; all that was seen was the "striae" due to the differences of refractive index of the solution and the titrant. This continued until the position corresponding with the addition of 1·50 equivalents of acid per sodium tungstate molecule was reached. Thereafter, the addition of acid caused the solutions to become opalescent, and precipitation of white tungstic oxide took place within a short time. The solution that had been 0·2 M

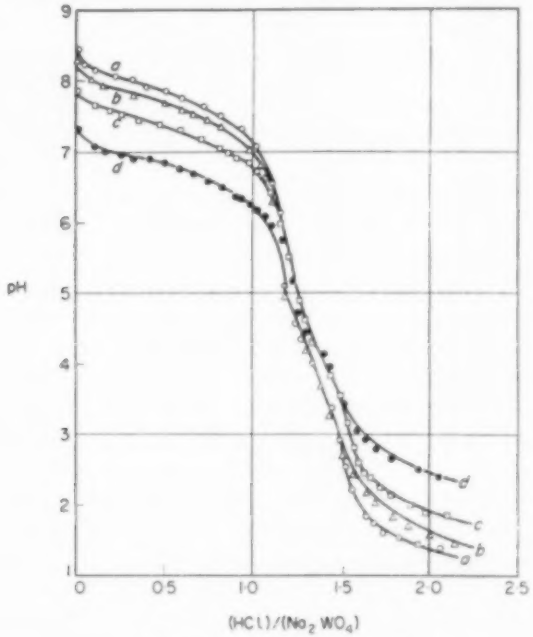

FIG. 1.—Glass electrode titrations of
a. 50 ml 0·200 M Na_2WO_4 with 4·133 M HCl
b. 50 ml 0·100 M Na_2WO_4 with 4·133 M HCl
c. 50 ml 0·0500 Na_2WO_4 with 1·178 M HCl
d. 50 ml 0·0100 M Na_2WO_4 with 0·4133 M HCl.

sodium tungstate deposited 90 per cent of its tungstic oxide within one day of the addition of two equivalents of hydrochloric acid per sodium tungstate molecule. Opalescence was also observed in the solution which had been 0·05 M sodium tungstate, but it did not develop for 3 hr. The most dilute solution exhibited neither opalescence of precipitation during the titration, and no turbidity was seen for up to one week after the titration, the final pH of the solution being 2·3. The effect of increasing the time allowed between the addition of the titrant and the measurement of pH value was noticeable only in that portion of the curve which lay between the two inflexions; a typical case is shown on Fig. 4, curve 6, in which the inflexion at 1·14 equivalents of acid becomes weaker as more time is allowed, and that at 1·50 equivalents, more pronounced. The rate of change of the values is small, and the higher values noted were recorded after one day in each case.

Conductometric titrations. All four titration curves possess two rectilinear branches, the break between the branches falling at the position corresponding with the addition of 1·50 equivalents of hydrochloric acid per sodium tungstate molecule. The major portions of the curves are separated by a gently rising portion, which decreases in size with increasing dilution of the solution paralleling increasing weakness of the electrometric inflexions at [HX] : [WO_4''] ca· 1·14.

The observed values of conductivity have been compared with certain calculated values as listed in Table 1.

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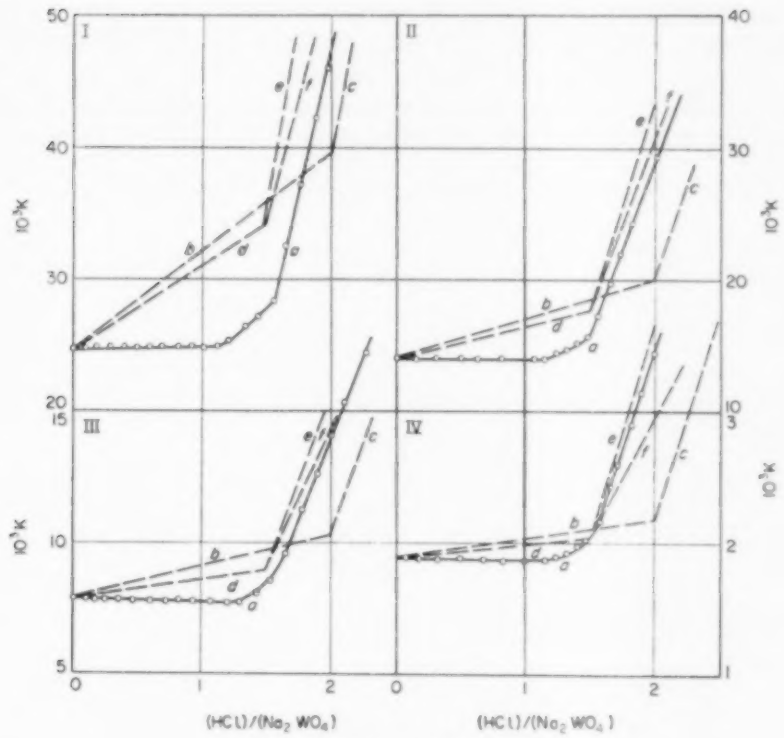

FIG. 2.—Conductometric titrations of
I. 50 ml 0·200 M Na_2WO_4 with 4·133 M HCl
II. 50 ml 0·100 M Na_2WO_4 with 4·133 M HCl
III. 50 ml 0·0500 M Na_2WO_4 with 1·178 M HCl
IV. 50 ml 0·0100 M Na_2WO_4 with 0·4133 M HCl.
The solid lines with open circles represent curves fitted to experimental data: the dotted lines indicate values of conductivity calculated for the reactions listed in Table 1.

TABLE 1.—THE REACTIONS FOR WHICH THE VALUES OF CONDUCTIVITY ARE RECORDED ON FIG. 2.

Curve	Reaction for which the values are plotted
a	Observed values from titrations.
b	$Na_2WO_4 2HCl \rightarrow WO_3 + H_2O + 2NaCl(WO_3$ non-conducting).
c	Addition of HCl to solution of NaCl, concentration and volume corresponding with that obtaining at the end of reaction *b*.
d	$4Na_2WO_4 + 6HCl \rightarrow Na_2O(WO_3)_4 + 6NaCl + H_2O$.
e	Addition of HCl to solution containing $Na_2O(WO_3)_4$ and NaCl.
f	$Na_2O(WO_3)_4 + 2HCl \rightarrow H_2O(WO_3)_4 + 2NaCl$.

(The values for the conductivity of sodium tungstate and sodium tetratungstate are taken from the data in the *International Critical Tables*, and from direct measurements at this time. The values for the addition of hydrochloric acid to sodium chloride solution were also directly measured.)

DISCUSSION

The observed titration results form a bridge between those of BRITTON and GERMAN[1] and of JANDER *et al.*,[5,6] the small differences between the latter now being seen to be due to the fact that the investigators worked in different concentration ranges. The conductometric data confirm the existence of a solute of

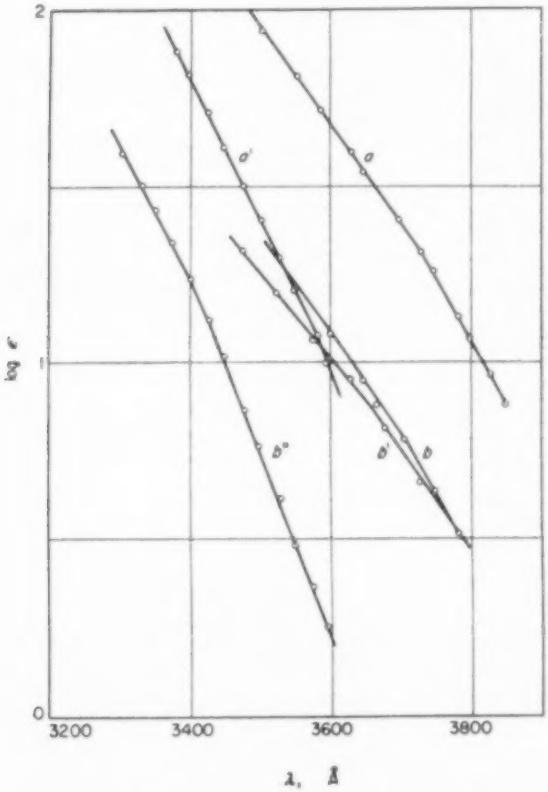

FIG. 3.—Ultra-violet absorption spectra of
a. 0·0100 M Na_2WO_4 + 1·14 equivalents of HCl per Na_2WO_4 molecule (spectrum taken 15 min after solutions were mixed)
a^1. *a* after 24 hr interval
b. 0·0500 M Na_2WO_4 + 1·14 equivalents of HCl per Na_2WO_4 molecule (spectrum taken immediately)
b^1. *b* after 20 min
b^{11}. *b* after 24 hr interval.

empirical formula $Na_2O(WO_3)_4nH_2O$, which behaves as the sodium salt of a strong acid: The data and the observed events point to the existence of a solute $Na_2O(WO_3)_{2\cdot33}nH_2O$ which is not stable with time, and which cannot be reformed by the addition of alkali to tetratungstate. The ultra-violet absorption spectra show that the solution at [HX] : [Na_2WO_4] equal to 1·14 (acidification) does not obey Beer's Law, and that the optical density decreases with time. This would indicate that at this ratio the solutions contain comparatively large particles which increase in size with time. Acidified tungstate solutions have therefore at least one of the properties of

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dispersions. This is in agreement with BETTINGER and TYREE.[9] However, solutions of the same tungstate concentrations in which [HX] : [Na_2WO_4] is 1·50 exhibit much smaller variations in their optical properties, confirming the presence of a stable ionic species at this solution composition. The electrometric data indicate the strong concentration dependence of the phenomena at [HX] : [Na_2WO_4] equal to 1·14: Fig. 4

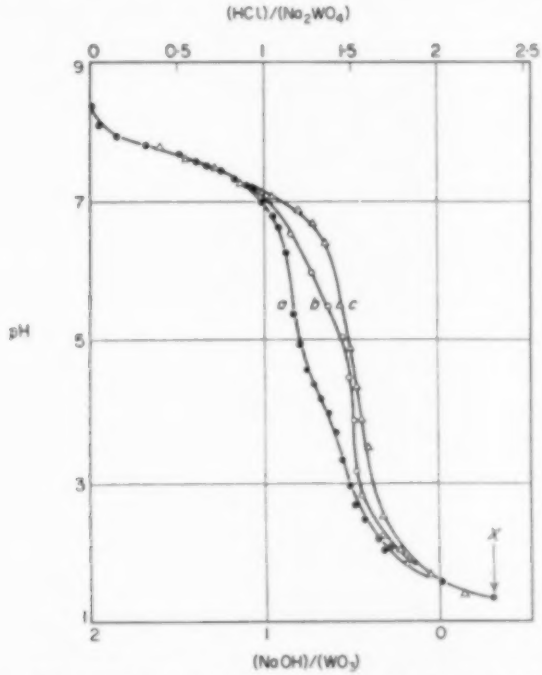

FIG. 4.—Glass electrode titrations of 50 ml 0·100 M Na_2WO_4 with
a. 4·133 M HCl, 5 min being allowed between each reading
b. 4·133 M HCl, 20 min between each reading
c. solution *a* titrated with 4·026 M from the position *X*.

demonstrates how rapidly the electrical properties of the unstable species are eliminated. Curve *b*, Fig. 4 shows the pH values observed in a concentrated solution when 20 min were allowed between readings. The inflection at [HX] : [Na_2WO_4] equal to 1·14 has essentially disappeared, and the pH values in that range (between pH 7 and pH 3) are markedly different (the optical properties are much slower to change). However, the pH set up after the addition of 1·5 equivalents of acid is but little changed. The solution *a* (Fig. 4.) was backtitrated from the position "*X*" with sodium hydroxide solution, and the curve *c* was obtained. The values observed were stable with time, except at pH values greater than 8, where initially higher values dropped to the curve shown within an hour. The values passed smoothly through the position [HX] : [WO_4''] equal to 1·14.

It is concluded that previous conflicting interpretations of data in this system can be resolved on the basis of the concentration-dependent presence of (unstable) species

[9] D. J. BETTINGER and S. Y. TYREE, JR., *J. Amer. Chem. Soc.* **79**, 3355 (1957).

intermediate in composition between "ortho" and "meta" tungstate. In addition, it seems likely that light absorption and scattering measurements will be more sensitive to the changes occurring in the system than will any electrometric measurement.

Acknowledgements—I am grateful to the Senate and Council of the University of Exeter, the Ministry of Education of H.M. Government and the Foundation Governors of King Edward VI School, Totnes, for the award of scholarships.

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PHOTOSUBSTITUTION REACTIONS OF SOME Cr(III) COMPLEXES*

A. W. ADAMSON
Department of Chemistry, University of Southern California
Los Angeles, California

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Abstract—The ion $Cr(H_2O)_6^{3+}$ is found to undergo second order photochemical substitution reactions with thiocyanate and chloride ions, and, likewise, $Cr(NH_3)_5(H_2O)^{3+}$, with thiocyanate ion. Quantum yields for the forward and reverse reactions are given for the wavelength region 400 to 575 $m\mu$, and, for the first system, at several temperatures. It is suggested that the mechanism for the second order processes involves formation of an ion pair which then undergoes a photochemical outer-inner sphere exchange of ligands. An evaluation is made of the evidence bearing on the exact nature of the photoactivated state involved.

From a study of the reverse or photoaquation reactions, in the case of the thiocyanate containing systems, it is possible to calculate the pseudo equilibrium constants for the photostationary states obtained after long irradiation. Since these are wavelength dependent, the systems are photochromic in nature and may have some useful applications.

IT has been shown that the photochemical behaviour of Co(III) complexes can be understood in terms of a redox type of intermediate which could either return to the original species or react unimolecularly to give either redox or aquation products.[1,2,3] The postulation of such an intermediate served to explain why the quantum yields for photoredox reactions correlated well with the ease of the corresponding thermal processes, while those for photoaquation did not.

The behaviour of Cr(III) complexes differs from that of the analogous Co(III) species in that only photoaquation and (more recently)[4] photoracemization reactions have been observed. While these findings can be accommodated by the above mechanism, SCHLÄFER[5] and especially PLANE and co-workers,[6,7] have attributed much importance to the doublet state of Cr(III) complexes as a long-lived intermediate capable of undergoing substitution reactions. Both mechanisms suggest that it should be possible to observe second order photosubstitution reactions, i.e. reactions other than aquation, and it was with this possibility in mind that the present study was undertaken. Cr(III) rather than Co(III) systems were chosen to eliminate the complication of competing redox processes and with the hope that some evaluation of the role of the doublet state would be possible.

* Presented at the International Conference on Co-ordination Chemistry, London, April, 1959.

(1) A. W. ADAMSON and A. H. SPORER, *J. Inorg. Nucl. Chem.* **8**, 209 (1958).
(2) A. W. ADAMSON and A. H. SPORER, *J. Amer. Chem. Soc.* **80**, 3865 (1958).
(3) A. W. ADAMSON, To be presented 136th Meeting of the American Chemical Society, Atlantic City, September, 1959.
(4) A. W. ADAMSON and S. SPEES, Abstracts of the International Conference on Co-ordination Chemistry, London (1959).
(5) H. L. SCHLÄFER and O. KLING, *J. Inorg. Nucl. Chem.* **8**, 320 (1958).
(6) R. A. PLANE and J. P. HUNT, *J. Amer. Chem. Soc.* **79**, 3343 (1957).
(7) M. R. EDELSON and R. A. PLANE, *J. Phys. Chem.* **63**, 327 (1959).

EXPERIMENTAL

Materials and analytical procedures. The compound $[Cr(H_2O)_6][ClO_4]_3$ was prepared first by the procedure described by POSTMUS and KING[8]. The moist solid obtained was made up to a stock solution which was ca. 1 M in Cr(III) and 0·5 M in perchloric acid. Actual concentrations were determined by the procedures referred by these authors. This stock solution will be referred to as solution A. The procedure involves the formic acid reduction of chramic oxide and in the preparation of solution A a slight excess of the former was used. Later, a second preparation was made, leading to stock solution B, which followed the more detailed instructions of GATES[9] which insured the presence of a slight excess of Cr(VI) prior to crystallization out of the product. The two preparations gave identical spectra, except that solution B showed a well defined peak at 260 mμ while A showed only a shoulder; this difference is attributed to the presence of some Cr(II) in solution A.

Solutions of $Cr(H_2O)_5NCS^{2+}$ were prepared by equilibrating a solution 0·050 formal in $Cr(H_2O_6^{3+})$, 0·15 formal in potassium thiocyanate and 0·010 formal in perchloric acid, followed by an ion-exchange separation according to KING and DISMUKES[10]. The Cr(III) content and absorption spectra were measured for several fractions of the eluate (1 M perchloric acid solution, leading to average apparent extinction coefficients of 31·1, 32·8 and $2{\cdot}76 \times 10^3$ at the absorption maxima at 570, 410 and 292 mμ, respectively. By comparison, the corresponding literature values are 31·5, 33·6 and $2{\cdot}90 \times 10^3$, respectively[8,10].

$[Cr(NH_3)_5(H_2O)][ClO_4]_3$ was prepared as previously described[11] and its purity checked by comparison of the absorption spectrum with that of an analysed sample. Other chemicals used were of Reagent quality, and solutions were standardized by conventional methods.

The rates of formation of $Cr(H_2O)_5(NCS)^{2+}$, $Cr(NH_3)_5(NCS)^{2+}$ and of $Cr(H_2O)_5Cl^{2+}$ were determined spectrophotometrically using the following respective values for the extinction coefficients and wavelengths: $2{\cdot}90 \times 10^3$ (292 mμ), $3{\cdot}35 \times 10^3$ (295 mμ) and 245 (230 mμ). The large values of the first two made accurate determinations of small amounts of reaction possible, but in the last case it was difficult to obtain enough photolysis for good accuracy. The aquation of $Cr(H_2O)_5(NCS)^{2+}$ was following by adding aliquots to an excess of a ferric perchlorate reagent[11] and determining the amount of free thiocyanate ion spectrophotometrically. The extinction coefficient, per thiocyanate in the iron complex, was $4{\cdot}35 \times 10^3$ (450 mμ) under the conditions employed. A Cary recording spectrophotometer was used for obtaining the visible and U.V. absorption spectra, and a Beckman DU instrument for the analytical measurements.

Procedures for the rate measurements. The general procedure consisted of preparing a solution of desired composition, placing half in a volumetric flask which was kept (in the dark) in a thermostat bath, and using the other half for the photochemical runs. Since only small amounts of reaction were involved, the differences between the extents of reaction in the two solutions at various times were taken as due to the photochemical process. Some data showing the dark reaction and the net photochemical reaction at several temperatures are shown in Fig. 1 for the $Cr(H_2O)_6^{3+}$–SCN^- system.

The photochemical runs were carried out using the same general equipment previously described[1,2] and the same method for determining the intensity of absorbed light. An important modification, however, was that the irradiations were made in a thermostated cell. The inner, cylindrical compartment of the cell contained the solution being studied, and this was kept to within 0·1°C of the desired temperature by circulating thermostated water through the surrounding jacket. Since the irradiating beam had to pass through the cell to the bolometer, both the inner compartment and the jacket were provided with parallel, optically flat Pyrex windows. The bolometer readings, which were precise to a few per cent, were used only for relative intensity measurements. Absolute quantum yields were obtained by calibration with standard actinometric solutions. Wavelength selection was accomplished by the use of one or the other of two glass filters. The window for filter 1 lay between 350 and 450 mμ and, for filter 2, from 540 mμ to beyond 700 mμ. By rough juxtaposition of these windows and the absorption spectra of the initial species, most of the light absorption occurred at ca. 400 mμ and 575 mμ, in the case of $Cr(H_2O)_5^{3+}$, and at 370 and 560 mμ, in the case of $Cr(NH_3)(H_2O)^{2+}$, using filters 1 and 2, respectively.

Calculation of τ values. Fluorescence life-times were calculated by means of the equation given by

[8] C. POSTMUS and E. L. KING, *J. Phys. Chem.* **59**, 1208 (1955).
[9] H. S. GATES, Thesis, University of Wisconsin (1956).
[10] E. L. KING and E. B. DISMUKES, *J. Amer. Chem. Soc.* **74**, 1674 (1952).
[11] A. W. ADAMSON and R. G. WILKINS, *J. Amer. Chem. Soc.* **76**, 3379 (1954).

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LEWIS and KASHA[12]. In order to separate the doublet absorption from the tail of the nearest main band, the spectrum in each case was plotted as log ϵ vs. $(\Delta\nu)^2$ where $\Delta\nu$ was the difference between the particular wave number and that of the peak of the nearest *main* absorption band. Since the main band had the approximate shape of a gaussian error curve[13] absorption due to the doublet state appeared as a positive departure from an otherwise linear plot. This departure was then plotted as a function of ν so as to evaluate the required integral, $\int \epsilon \, d\nu$.

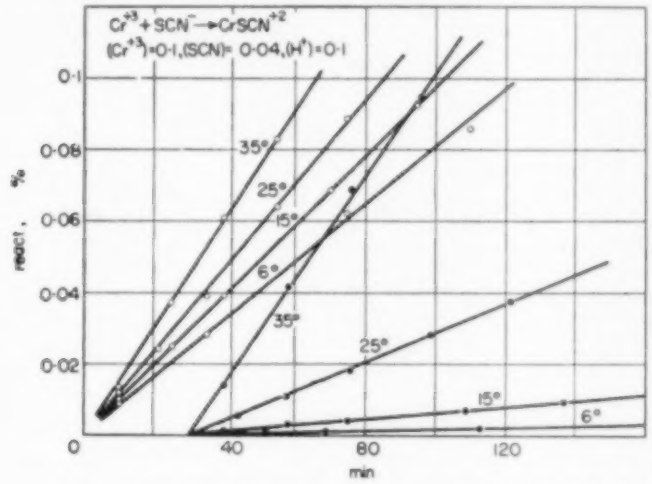

FIG. 1.—Photochemical and dark reaction of SCN^- with $Cr(H_2O)_6^{3+}$
Conditions: 0·100 M complex (solution A), 0·0400 M SCN^-, 0·100 M $HClO_4$; ●—dark reaction (time scale shifted); ○—photochemical reaction at 575 mμ, absorbed light intensity $3{\cdot}6 \times 10^{-4}$ Einsteins per min per 25 ml volume

RESULTS

The most complete and accurate data were obtained for the $Cr(H_2O)_6^{3+}$-SCN^- system, and these will be covered first. As noted under *Experimental*, two preparations of the Cr(III) stock solution were used. For both solutions neither the photochemical nor the dark reaction deviated detectably in stoichiometry from the equation:

$$Cr(H_2O)_6^{3+} + SCN^- = Cr(H_2O)_5NCS^{2+} + H_2O \qquad (1)$$

There was, however, some difference in reaction rate. Some of the results for stock solution A are given in Table 1. It is seen, firstly, that both the apparent quantum yield, ϕ_1 and the second order specific rate constant, k_1, showed little dependence on hydrogen ion concentration. This was to be expected since in the region of acidity employed there should have been little contribution from the hydrolytic path noted by POSTMUS and KING.[14] The effect of ionic strength was not large, and was more apparent for k_1 than for ϕ_1, in the former case, the variation with μ agreed well with that found by POSTMUS and KING (e.g. if plotted according to their Fig. 2). Finally, it is seen that ϕ_1 was first order in thiocyanate and independent of Cr(III) concentrations. This corresponds to second order overall kinetics since ϕ_1 is based on the absorbed light which was entirely due to the Cr(III) present.

The absolute magnitude of k_1 was about twice that found by POSTMUS and KING, however, and it seems clear that this was due to catalysis by the Cr(II) probably

[12] G. N. LEWIS and M. KASHA, *J. Amer. Chem. Soc.* **67**, 994 (1945).
[13] K. JORGENSEN, *Acta Chem. Scand.* **8**, 1495 (1954).
[14] C. POSTMUS and E. L. KING, *J. Phys. Chem.* **59**, 1216 (1955).

present in preparation A. In confirmation of this explanation, addition of a small amount of Cr(II) solution did in fact markedly increase both k_1 and ϕ_1. This type of catalysis has been reported before for thermal reactions[15] (although not for photochemical ones).

TABLE 1.—PHOTOCHEMICAL AND THERMAL REACTION OF $Cr(H_2O)_6^{3+}$ WITH SCN^-*

Concentrations (M)			Ionic strength	Quantum yield ($10^4\phi_1$)	Rate constant 10^4k_1 (M^{-1} min^{-1})
Cr(III)	$HClO_4$	Other			
0·100	0·100	0·0400 SCN^-	0·74	1·1	2·32
0·100	0·100		0·72	0·65	2·46
0·100	0·100	$NaClO_4$	1·7	0·58	1·96
0·100	0·100	$NaClO_4$	2·2	0·60	1·94
0·200	0·100		1·3	0·65	1·84
0·0500	0·100	$NaClO_4$	0·70	0·50	2·35
0·100	0·200		0·80	0·54	1·87
0·100	0·49		1·1	0·48	1·84
0·100	0·100	ca. 0·004 Cr(II)	0·7	0·80	11·3

* Conditions (unless otherwise specified): 25°C, 575 mμ, 0·0200 M SCN^-

The remaining experiments were made using Cr(III) stock solution B, for which, as is seen below, the k_1 values obtained were in close agreement with those of POSTMUS and KING. Solution B also gave somewhat lower quantum yields than did A. The

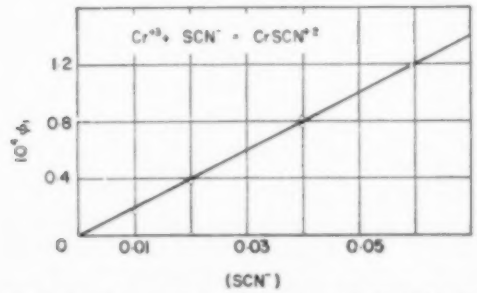

FIG. 2.—Photochemical reaction of SCN^- with $Cr(H_2O)_6^{3+}$—Dependence of ϕ_1 on SCN^- concentration at 25°C and 575 mμ.†

dependence of ϕ_1 on thiocyanate concentration was redetermined, with the results shown in Fig. 2, indicating first order dependence and a negligible amount of any thiocyanate independent path. These results as well as those for the reverse reaction, i.e. the photochemical aquation of $Cr(H_2O)_5(NCS)^{2+}$, are summarized in Table 2 for the two wave lengths studied. For the forward reaction, quantum yields are reported as ϕ_1' values, where $\phi_1 = \phi_1'$ (SCN).

The temperature dependencies are shown in Fig. 3. Firstly, for the dark reaction the activation energy for k_1 was 24·6 kcal, in fair agreement with that of 25·7 reported

† *Note added in proof:* Divide all ϕ values by 4·5.

[15] F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*. John Wiley, New York (1958).

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TABLE 2.—SUMMARY OF RESULTS FOR THE $Cr(H_2O)_6^{3+}$—SCN^- SYSTEM

Dark reaction			Photochemical reaction		
Quantity	POSTMUS and KING	Present	Quantity	575 mμ	400 mμ
k_1 ($M^{-1}min^{-1}$ (25°C)	1.07×10^{-4} ($\mu = 0.5$)	1.05×10^{-4} ($\mu = 0.7$)	ϕ_1' (25°C)	2.0×10^{-3} ($\mu = 0.7$)	0.24×10^{-3} ($\mu = 0.7$)
k_2 (min^{-1} (25°C)	5.5×10^{-7} ($\mu = 0.5$)	5.3×10^{-7} ($\mu = 0.4$)	ϕ_2 (25°C)	0.93×10^{-4} ($\mu = 0.4$)	0.27×10^{-3} ($\mu = 0.4$)
K (25°C)	195 ($\mu = 0.5$)	197†	K_s (25°C)	9.3	4.2*
E_1(kcal)	25.7 ($\mu = 0.08$)	24.6 ($\mu = 0.7$)	E_1	3.5 ($\mu = 0.7$)	3.5 ($\mu = 0.7$)
E_2(kcal)	28.1	—	E_2	6.1 ($\mu = 0.4$)	8.3 ($\mu = 0.4$)
ΔH(kcal)	−2.4		ΔH_s	−2.6	−4.8

* Estimated K_s at 290 mμ: 5×10^{-3}. (†) Based on the present k_1 and k_2 values, at $\mu = 0.7$ and 0.4, respectively.

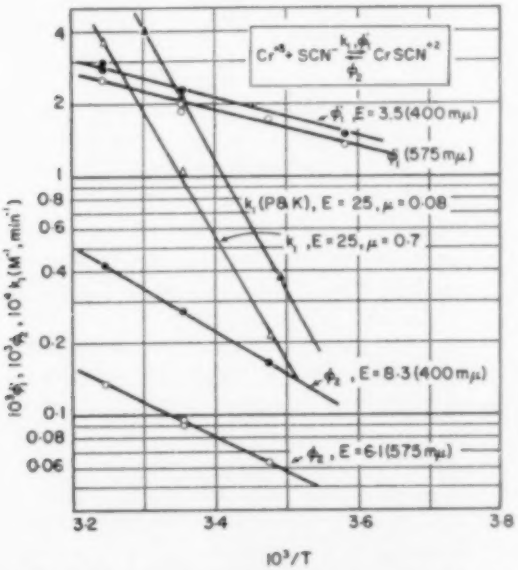

FIG. 3.—$Cr(H_2O)_6^{3+}$–SCN^- system—Temperature dependence of k_1, ϕ_1', and ϕ_2. △–k_1 for dark reaction, present data ($\mu = 0.70$); ▲—k_1 for dark reaction, reference 8 ($\mu = 0.08$); ●, ○ (upper lines), ϕ_1' at 400 and 575 mμ, respectively; ●, ○ (lower lines), ϕ_2 at 400 and 575 mμ, respectively. (Solution B used).‡

‡ *Note added in proof*: Divide all ϕ values by 4.5.

by POSTMUS and KING. The two sets of data also agree well in absolute magnitude, if correction is made for the difference in ionic strength involved. For the photochemical reaction, the values of ϕ_1' were very nearly the same for the two wavelengths involved so that in both cases the apparent activation energy was 3·5 kcal.

With respect to the aquation reaction, not only were the ϕ_2 values larger at the shorter wave length. but they also showed a slightly higher apparent activation

TABLE 3.—SUMMARY OF RESULTS FOR THE $Cr(NH_3)_5(H_2O^3)^+$–SCN^- SYSTEM*

Concentrations (M)			Ionic strength	Wavelength (mμ) $10^3\phi_1$	Quantum yield $10^3\phi_1$	Rate constant $(10^3k_2$ $(M^{-1}min^{-1})$
Cr(III)	SCN^-	Other				
0·0300	0·0200		0·21	560	1·5	1·67
0·0100	0·0200		0·090	360	3·5	2·09
0·0100	0·0400		0·11	360	5·3	2·04
0·0100	0·0200	$NaClO_4$	0·48	360	1·2	1·0
0·0100	0·0200	$NaClO_4$	1·08	360	0·60	0·72
0·0100	0·0200	$NaClO_4$	1·68	360	0·66	0·42
0·0100	0·0200	2 M Sucrose	(0·090)	360	0·67	6·4

* All runs at 25°C; the solutions were also 0·0100 M in perchloric acid.

energy, 8·3 vs. 6·1 kcal. The dark rate is quite small and was measured only at 35°C. The value of the first order rate constant was $2·5 \times 10^{-5}$ min^{-1} which, if corrected to 25°C by means of POSTMUS and KING's activation energy value, agrees well with their rate constant (see Table 2).

Results for the $Cr(NH_3)_5(H_2O)^{3+}$–SCN^- system are less complete; they are summarized in Table 3. Here, in contrast to the previous system, a quite considerable dependence of ϕ_1 and of k_1 on the concentration of sodium perchlorate was found. The effect is not viscosity related since both quantities were increased when 2 M sucrose was used as the solvent medium. Because of this effect of electrolyte content, it was difficult to interpret the dependence of ϕ_1 and k_1 on the thiocyanate concentration; it was approximately first order, however. Finally, a few experiments were made with the $Cr(H_2O)_6^{3+}$–Cl^- system. In this case the product absorbs only slightly more than does the reactant so that it was difficult to measure accurately the small amounts of reaction obtainable because of the low quantum yield.

A general summary for the three systems is given in Table 4. In the table, the values of ϕ_2 for the $Cr(NH_3)^5(H_2O)^{3+}$–SCN^- reaction are taken from reference (2), and that of K is obtained by combining the value of k_2 from reference (11) with the present value of k_1. Ion-pairing was evidently a possible factor affecting the behaviour of these systems and approximate values for K_{ip} are included in the table. The estimate for the $Cr(NH_3)_5(H_2O)^{3+}$–SCN^- case was obtained in the course of these investigations, since none was available in the literature. It was found that the optical density of solutions containing a fixed concentration of $Cr(NH_3)_5(H_2O)^{3+}$ and of perchloric acid was essentially independent of thiocyanate ion concentration for wavelengths in the visible, but increased with increasing concentration for wavelengths below about 320 mμ. Values of ΔD, the difference between the otpical density for

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the solution and that for the constituents separately, was most precisely determinable at about 274 mμ; they were found to be proportional to thiocyanate concentration up to 1M for solutions 0·01 M in complex, 0·01 M in perchloric acid and containing sufficient sodium perchlorate to keep the ionic strength at 1·07. This linearity set an upper limit to K_{ip} of about 0·2, making a liberal allowance for experimental error, including the difficulty, at the higher thiocyanate concentrations, of correcting for the net substitution reaction which made the optical densities time dependent. The

TABLE 4.—PHOTOCHEMICAL SUBSTITUTION REACTIONS

System	K (25°C)	K_{ip} (25°C)	Photochemical behaviour at 25°C				
			mμ	ϕ_1'	ϕ_2	K_s	ϕ_{ip}
$Cr(H_2O)_6^{3+}$–SCN^-	197	⟨0·1[16]	575	$2·0 \times 10^{-3}$	$0·94 \times 10^{-4}$	9·3	0·020
			400	$0·24 \times 10^{-3}$	$0·27 \times 10^{-3}$	4·2	0·022
$Cr(H_2O)_6^{3+}$–Cl^-	0·2[9]	1·5[9]	370	$6·5 \times 10^{-3}$	—	—	0·0045
$Cr(NH_3)_5(H_2O)^{3+}$ –SCN^-	$1·2 \times 10^4$	—	560	0·075 (μ = 0·21)	0·013 (μ = 0·08)	3·8	—
		0·2 (μ = 1·07)	360	0·029 (μ = 1·08)	0·018 (μ = 0·07)	1·08	0·13

ΔD values themselves were ionic strength dependent, however, and the matter of attempting any more accurate determination of K_{ip} was considered inadvisable.

DISCUSSION

The present findings can be explained in terms of either of two mechanisms, which can be called complex intermediate and ion-pair intermediate, respectively. In somewhat general form, these are as follows.

1. *Complex intermediate*:

$$CrA_5(H_2O)^{3+} \underset{k_{1d}}{\overset{h\nu}{\rightleftharpoons}} [CrA_5(H_2O)^{3+}]^* \tag{2}$$

$$[CrA_5(H_2O)^{3+}]^* + X^- \xrightarrow{k_{1r}} CrA_5X^{2+} + H_2O \tag{3}$$

Here, k_{1d} and k_{1r} denote the rate constants for deactivation and for further reaction of the intermediate, which could either be an activated electronic state such as the doublet or a chemical intermediate, e.g. of the redox type postulated for Co(III) complexes.

2. *Ion-pair intermediate*:

$$CrA_5(H_2O)^{3+} + X^- \underset{}{\overset{K_{ip}}{=}} [CrA_5(H_2O)^{3+}][X^-] \tag{4}$$

$$[CrA_5(H_2O)^{3+}][X^-] \underset{k_{1d}}{\overset{h\nu}{\rightleftharpoons}} [CrA_5(H_2O),X]^{2+} \tag{5}$$

$$[CrA_5(H_2O),X]^{2+} \xrightarrow{k_{1r}} CrA_5X^{2+} + H_2O \tag{6}$$

[16] A. L. PHIPPS and R. A. PLANE, *J. Amer. Chem. Soc.* **79**, 2458 (1957).

The intermediate in this case is written in ambiguous form to avoid unnecessary commitment as to its structure; it could be regarded as a seven co-ordinated doublet state (see discussion at end of reference (7) or as a purely chemical intermediate.

Both mechanisms show a deactivation or return process given by k_{1d}; some such provision is necessary in order to account for quantum yields less than unity. They differ in the supposed nature of the species that is activated by light absorption and while no definite decision seems possible, there is some basis for favouring the second mechanism.

According to Mechanism 2 the apparent quantum yield ϕ_1 cannot exceed the fraction of complex present as ion-pairs; alternatively, ϕ_{ip} cannot exceed unity where

$$\phi_1' = \phi_{ip} K_{ip} \tag{7}$$

If mechanism 1 applies, however, ϕ_1 would

$$\phi_1 = \frac{k_{1r}(X^-)}{k_{1r}(X^-)} + k_{1d} \tag{8}$$

and could be as high as unity. The very low values found for ϕ_1 (e.g. in Table 2) while consistent with either mechanism are more understandable in terms of mechanism 2. Specifically, the estimated values of ϕ_{ip}, shown in Table 4, seem quite reasonable.

An additional argument in favour of mechanism 2 is that the ion-pair path has been proven in the case of at least one thermal substitution reaction, $Co(NH_3)_5(H_2O)^{3+}$–SO_4^{-2},[17] and there is much additional evidence for specific anion effects on substitution reactions rates which are best explained in terms of an ion-paired intermediate.[11,15] In this connection, it is perhaps significant that quite different ionic strength effects were noted for the $Cr(H_2O)_6^{3+}$–SCN^- case than for the $Cr(NH_3)_5(H_2O)^{3+}$–SCN^- one. This again suggests that ion-pairing rather than general interionic attraction effects are important. Another qualitative point is that if Mechanism 1 prevailed, the intermediate might be expected to be quite short-lived, judging from PARKER and HATCHARD's observation that there were no transient intermediates in the flash photolysis of $Cr(C_2O_4)_3^{3-}$ of longer life than 15 μ sec[18] (this complex is known to photoracemize).[4] Any very short-lived species reacting according to Mechanism 1 should show a diffusion controlled rate and hence a solution viscosity dependence. This is contrary to what was observed when 2 M sucrose was used as the solvent (Table 3).

Assuming the ion-pair Mechanism 2 to apply, there remains the interpretation of the quantum yields and of their wavelength and temperature dependence. While no detailed conclusions seem possible, some analysis of the situation is helpful. The apparent activation energy as given by the temperature coefficient of ϕ_1', should correspond to the difference in activation energies for k_{1r} and k_{1d} (for small ϕ_1' values and recognizing that the heat of ion-pairing is generally small.[9,16] Similarly for the reverse or equation process. Thus for the $Cr(H_2O)_6^{3+}$–SCN^- system

$$E_1 = E_{\text{reaction}} - E_{\text{deactivation}} = 3{\cdot}5 \text{ kcal}$$
$$E_2 = E'_{\text{reaction}} - E'_{\text{deactivation}} = 8{\cdot}3 \text{ kcal (400 m}\mu\text{)}$$
$$6{\cdot}1 \text{ kcal (575 m}\mu\text{)}$$

where the primes refer to the aquation case.

[17] H. TAUBE and F. A. POSEY, *J. Amer. Chem. Soc.* **75**, 1463 (1953).
[18] C. A. PARKER and C. G. HATCHARD, *J. Phys. Chem.*, **63**, 22 (1959).

From the values for ϕ_{i_p} and for ϕ_2 and for E_1 and E_2 it is possible to calculate the ratio of the frequency factors for the reaction and deactivation steps for forward and reverse processes, i.e. $A_{\text{reaction}}/A_{\text{deactivation}}$. On doing this one obtains a value of forty for the forward reaction and values of 1500 and fifteen for the aquation reaction, at 400 and 574 mμ, respectively. In other words, the deactivation processes are hindered by factors of ten to a thousand over those leading to reaction; qualitatively, this is a consequence of the quantum yields being higher than expected in terms of the activation energies observed.

The size of these hindrance factors suggests that the intermediate $[CrA_5(H_2)O,X]^{3+}$ differs structurally from its precursor, and their wavelength dependence, that more of a loose succession of states is involved than some single well defined species. It is difficult, however, to decide whether or not the intermediate should be identified with a doublet state. It is true that we have found quantum yields to remain high when wavelengths in the doublet region are used. Thus for Reinecke's salt, the quantum yield for photo-aquation is 1·33 at 370 mμ[1,2] and 0·88 at 695 mμ[4]; also there is little change in the quantum yield of ca. 0·2 for the photoracemization of $Cr(C_2O_4)_3^{3-}$ over this wavelength region.[4] It can be argued from this that the doublet state is photochemically active and that this confirms its importance in general as an intermediate. It would be more convincing, however, if an actual rise in quantum yield could be observed in the 700 mμ region since the doublet bands appear as shoulders or, at best, weak peaks superimposed on the broad tail of the nearest main absorption band and it is hard to assess just how much the doublet mode of excitation contributes to the total absorption.

Among the other lines of reasoning used to support the importance of the doublet state is that of EDELSON and PLANE.[7] They consider the deactivation process to involve a thermal re-excitation of the doublet to the nearest quartet state, i.e. that $E_{\text{deactivation}}$ corresponds to the difference in $h\nu$ values for the two bands. The higher quantum yield for the photoaquation of $Cr(NH_3)_6^{3+}$ over that for water exchange with $Cr(H_2O)_6^{3+}$ was then attributed to the larger $\Delta(h\nu)$ for the former system and consequently smaller k_{1d} value. This line of reasoning is at best qualitative since it is based on the assumption that E_{reaction} is the same for photochemical reactions involving different Cr(III) complexes. Quite apart from this approximation, however, there does not seem actually to be any general correlation between $\Delta(h\nu)$ and quantum yield. Data illustrating this point are summarized in Table 5. Thus, for example, the quantum yield for the photoaquation of $Cr(NH_3)_5(NCS)^{2+}$ is seventy times that for $Cr(H_2O)_5(NCS)^{2+}$, although $\Delta(h\nu)$ is 15 kcal for the former and only 8·5 for the latter. Nor is there any correlation between ϕ and the fluorescence lifetime, τ, of the doublet state.

In summary, while it seems reasonable that the second-order photosubstitution reactions observed here involve an outer-inner sphere exchange of ligands, it is not possible to make a decision as to the exact nature of the active intermediate formed following light absorption. Possibly flash photolysis studies of these systems would help.

To consider another aspect of the present investigations, it is of interest to inquire into the nature of the photostationary state that should result from continued irradiation. For simplicity, the slow formation of further substitution products in the $Cr(H_2O)_6^{3+}$–SCN^- and $-Cl^-$ systems and the slow hydrolytic decomposition of

$Cr(NH_3)_5(H_2O)^{3+}$ will be ignored. Since the only absorbing species are then the reactant and product complexes, the forward and reverse rates may be formulated as follows:

$$R_f \propto I_0[\phi_1'\varepsilon_1(CrA_5(H_2O)^{3+})(X^-)] \quad (9)$$

$$R_b \propto I_0[\phi_2\varepsilon_2(CrA_5X^{2+})] \quad (10)$$

where ε_1 and ε_2 denote the extinction coefficients for the two complexes. At the photostationary state, $R_f = R_b$, giving a pseudo equilibrium constant, K_s:

$$K_s = \phi_1'\varepsilon_1/\phi_2\varepsilon_2 \quad (11)$$

Equations (9) and (10) assume a somewhat more complicated form if appreciable reduction in light intensity is occurring,[19] although (11) remains the same. Also,

TABLE 5.—SPECTRA VS. PHOTOCHEMISTRY OF Cr(III) COMPLEXES

Complex	Absorption bands (wave nos.)		$\Delta(h\nu)$ (kcal)	$10^3\tau$ (sec)	Reaction and ϕ	Ref.
	Doublet	Nearest quartet				
$Cr(NH_3)_6^{3+}$	15,300	21,500	17		aquation $\phi = 0{\cdot}3$	7
$Cr(NH_3)_5(H_2O)^{3+}$	15,200 16,300	20,900	16	3.4	aquation $\phi = 0{\cdot}3$	7
$Cr(NH_3)_5(NCS)^{2+}$	15,500	20,800	15	1·0	aquation $\phi = 0{\cdot}015$	1,2
$Cr(NH_3)_2(NCS)_4^-$	13,430 13,870 14,210	19,230	~15	49	aquation $\phi \simeq 0{\cdot}2$	1,2
$Cr(C_2O_4)_3^{3-}$	14,300	17,500	9·2	4·4	racemization $\phi = 0{\cdot}045$	4
$Cr(H_2O)_5(NCS)^{2+}$	14,600	17,500	8·5	7·6	aquation $\phi = 2 \times 10^{-4}$	
$Cr(H_2O)_6^{3+}$	15,000	17,420	7·0	7·0	O^{18} exch. $\phi = 0{\cdot}03$	6

it is assumed that the dark reaction can be neglected; if not, additional terms would be added to (9) and (10).[19]

The various K_s values are given in Tables 2 and 4. It is seen that they are appreciably wavelength dependent and would appear even more so had data for wavelenghs around 290 mμ been obtained (see estimate in Table 2) because of the rapid increase in the ratio of extinction coefficients for CrA^5X^{2+} vs. $CrA_5(H_2O)^{3+}$ at the smaller wavelengths.

It is thus evident that these systems are photochromic in the sense defined by HIRSHBERG[20]; they represent the first reported instances involving inorganic complexes. HIRSCHBERG described his studies of the similar behaviour of various fused

[19] G. ZIMMERMAN, L. CHOW and U. PAIK, *J. Amer. Chem. Soc.* **80**, 3528 (1958).
[20] Y. HIRSHBERG, *J. Amer. Chem. Soc.* **78**, 2304 (1956).

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ring systems as possibly providing photochemical memory models and it appears that the present findings could similarly be applied. The quantum yields found here are rather low, however, and it is likely that better examples will be found.

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INFRA-RED AND VISIBLE ABSORPTION STUDIES OF THE PENTACYANONICKELATE(II) ION IN AQUEOUS SOLUTION*

R. L. McCULLOUGH, L. H. JONES and R. A. PENNEMAN
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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Abstract—The infra-red spectra of aqueous solutions containing tetracyanonickelate(II) and excess cyanide ions show a single new absorption peak characteristic of the pentacyanonickelate(II) ion, $[Ni(CN)_5]^{3-}$. The growth of this new infra-red peak and the diminution of the known $[Ni(CN)_4]^{2-}$ absorption is described completely by the equilibrium: $[Ni(CN)_4]^{2-} + CN^- \leftrightharpoons [Ni(CN)_5]^{3-}$ over a cyanide concentration range 0·05–5 M. No infra-red absorption of a higher complex, e.g. $[Ni(CN)_6]^{4-}$ was detected even in nearly saturated NaCN and ~0·4 M $[Ni(CN)_4]^{2-}$. Infra-red absorption characteristics of the complex ions are:

$$[Ni(CN)_4]^{2-}, \epsilon = 1068 \pm 95 \text{ mole}^{-1} \text{ l. cm}^{-1} \text{ at } 2124 \pm 1$$

$$[Ni(CN)_5]^{3-}, \epsilon = 1730 \pm 230 \text{ mole}^{-1} \text{ l. cm}^{-1} \text{ at } 2102 \pm 2$$

Continuous variation experiments at 100 Å intervals from 3800 Å to 6000 Å showed only a 1 : 1 complex between CN^- and $[Ni(CN)_4]^{2-}$. From visible and infra-red absorption data the constant for the formation of $[Ni(CN)_5]^{3-}$ from $[Ni(CN)_4]^{2-}$ and CN^- was found to be 0·19 ± 0·01 l. mole^{-1} at 25·2° in solutions of constant ionic strength (μ = 1·34). The formation constant was determined at three temperatures over the range 15–35°, yielding a ΔH of ~ −3 kcal/mole. Magnetic measurements show that the pentacyanonickelate(II) ion is diamagnetic.

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INFRA-RED studies[1,2,3] of cyanide complexes of various metals in aqueous solution have yielded information on the following species: $Ag(CN)_2^-$, $Ag(CN)_3^{2-}$, $Ag(CN)_4^{3-}$, $Au(CN)_2^-$, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cu(CN)_4^{3-}$, $Hg(CN)^+$, $Hg(CN)_3^-$, $Hg(CN)_4^{2-}$, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$, and $Zn(CN)_4^{2-}$.

This paper presents a similar study of the cyanide complexes of Ni(II) in aqueous solution.

The square planar tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$ is well known and the properties of the hydrated potassium salt are given by GMELIN[4]. HUME and KOLTHOFF[5] as well as VRESTAL and HAVIR[6] report that the tetracyanonickelate(II) ion is very stable in aqueous solution. In agreement with these reports, we find that pure solutions of the tetracyanonickelate(II) ion are neutral and obey Beer's law over wide concentration ranges. The species $Ni(CN)_2$ precipitates from aqueous solutions whenever an attempt is made to remove a cyanide ligand from the complex by slight acidification.

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[1] L. H. JONES and R. A. PENNEMAN, *J. Chem. Phys.* **22**, 965 (1954).
[2] L. H. JONES and R. A. PENNEMAN, *J. Chem. Phys.* **24**, 293 (1956).
[3] L. H. JONES and R. A. PENNEMAN, Paper to be published on cyanide complexes of Zn, Cd, and Hg.
[4] GMELIN-FRIEDHELM (Editors), *Handbuch der Anorganischen Chemie* Vol. 5, Part 1, p. 135. Verlag Chemie G.M.b.h., Berlin (1927).
[5] D. N. HUME and I. M. KOLTHOFF, *J. Amer. Chem. Soc.* **72**, 4423 (1950).
[6] J. VRESTAL and J. HAVIR, *Chem. Listy* **50**, 1321 (1956).

A pale yellow aqueous solution of sodium tetracyanonickelate(II) becomes successively orange, red and deep red upon addition of sodium cyanide. The colour changes reversibly with temperature, i.e. lightens on heating and intensifies on cooling. The coloration of such a solution containing excess cyanide persists, on slow evaporation, until near dryness. However, as crystallization occurs, the solution begins to decolorize. Infra-red and optical examinations of the residue show the presence of NaCN and $Na_2Ni(CN)_4 \cdot 3H_2O$ only.

JOB and SAMUEL[7] interpreted these colour changes as evidence for the formation of hexacyanonickelate(II) ion, $[Ni(CN)_6]^{4-}$. Later, SAMUEL[8] conducted colorimetric experiments which he interpreted as substantiating the existence of the $[Ni(CN)_6]^{4-}$ ion.

In this present work, further evidence has been collected establishing the existence of a new ionic species in solutions of sodium tetracyanonickelate(II) and sodium cyanide. Contrary to SAMUEL, however, the present work shows that the new species is $[Ni(CN)_5]^{3-}$ rather than $[Ni(CN)_6]^{4-}$.

The pentacyanonickelate(II) ion has been briefly mentioned previously: NYHOLM[9] stated (without giving supporting data) that he and B. S. MORRIS conducted unpublished spectrophotometric studies which led to the conclusion that a 1 : 1 complex ion of $[Ni(CN)_4]^{2-}$ and CN^- is formed in aqueous solution. MARTEL and CALVIN[10] also propose that the species $[Ni(CN)_5]^{3-}$ would be formed in aqueous solutions of $[Ni(CN)_4]^{2-}$ and CN^-.

EXPERIMENTAL

Reagents and solutions

Sodium tetracyanonickelate(II) was prepared[11] by the precipitation of nickel dicyanide from nickel nitrate solution and the subsequent dissolution of the well-washed nickel dicyanide in a stoicheiometric quantity of sodium cyanide. Recrystallization yielded yellow, needle-like crystals of sodium tetracyanonickelate(II) with three waters of crystallization. The optical properties of the crystals agreed with those reported by BRASSEUR and DE RASSENFOSSE[12]. On dehydration of the material at 110° a weight loss was obtained corresponding to three waters of hydration. Since dehydration occurs slowly at room temperature when exposed to laboratory air, the analysed trihydrate crystals were kept bottled until just prior to weighing. Analysed sodium cyanide was used.

Stock solutions were prepared of sodium tetracyanonickelate(II), sodium cyanide, and sodium perchlorate. Solutions for spectrophotometric examination were prepared by taking aliquots of these stock solutions and adding sufficient sodium perchlorate to maintain the molar ionic strength at ~1·34. The cyanide in each solution was corrected for hydrolysis.

The solutions used for the continuous variation experiment were prepared by mixing aliquot portions of stock solutions of $[Ni(CN)_4]^{2-}$ and CN^- of equal concentration so that a constant total volume was maintained.

Instrumentation and technique

The spectral measurements were made in the visible region with a Cary Model 14 recording spectrophotometer utilizing Corex cells of length 1–5 cm. Typical absorption spectra for the visible regions are given in Fig. 1.

The temperature of the solutions was maintained by circulating constant temperature water through the cell compartment walls.

[7] A. JOB and A. SAMUEL, *C.R. Acad. Sci., Paris* **177**, 188 (1923).
[8] A. SAMUEL, *J. Chim. Phys.* **40**, 247 (1943).
[9] R. S. NYHOLM, *Chem. Rev.* **53**, 263 (1953).
[10] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds* p. 226. Prentice Hall, New York (1952).
[11] W. C. FERNELIUS and J. J. BURBAGE, *Inorganic Syntheses* Vol. 2, p. 227. McGraw-Hill, New York (1946).
[12] H. BRASSEUR and A. DE RASSENFOSSE, *Mem. Soc. Sci., Liege* [2], **4**, 397 (1941).

The spectral measurements in the infra-red region were made with a Model 112 Perkin-Elmer Infra-red Spectrometer using a lithium fluoride prism. Approximately 0·01 ml of an appropriate solution was placed between two calcium fluoride flats separated by a tantalum spacer. A typical spectrum of an aqueous solution containing $Na_2Ni(CN)_4$ and NaCN is given in Fig. 2. Separate spectral measurements of the respective pure solutions characterized the infra-red peaks indicated by CN^- and $[Ni(CN)_4]^{2-}$.

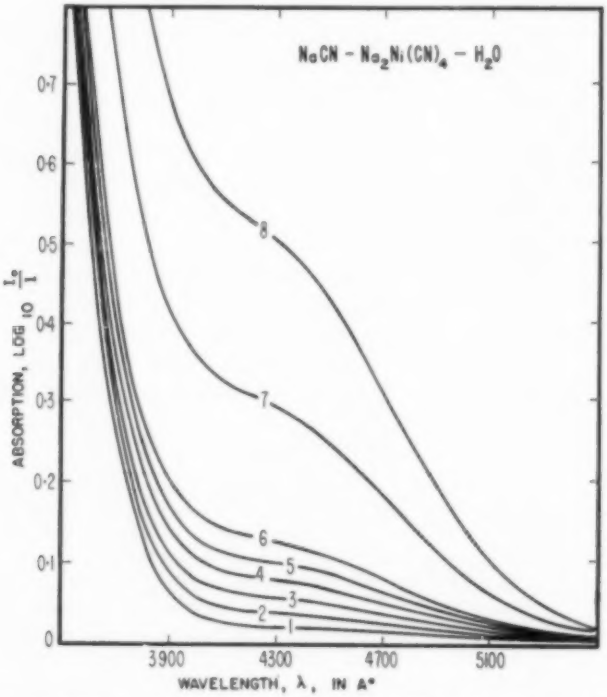

FIG. 1.—The visible absorption spectra of 0·050 M $[Ni(CN)_4]^{2-}$ and excess CN^- in 1 cm Corex cells at 25·2°. The ratio of the added cyanide concentration to the tetracyanonickelate(II) concentration corresponding to the individual curves is: (1) 5·8, (2) 8·1, (3) 10·0, (4) 11·9, (5) 14·0, (6) 15·6, (7) 28·8 and (8) 48·0.

The cell length was determined by measuring the thickness of the tantalum spacer and adding 5×10^{-4} cm (to compensate for the capillary film[11]).

RESULTS AND DISCUSSION

Characterization of the new species

Infra-red region. The strongest piece of evidence supporting the existence of a new species in solutions containing sodium tetracyanonickelate(II) and excess cyanide is the appearance of a new peak at 2102 cm^{-1} in the infra-red region (see Fig. 2). The variation of this new peak over a hundredfold range of cyanide concentrations (0·05 to 5·0 M) establishes its stoicheiometry as $[Ni(CN)_5]^{3-}$.

Visible region. (Continuous variations method) To verify in the visible region the stoicheiometric formula for the new complex obtained from the infra-red region,

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the method of "continuous variations" as set forth by JOB[13] and elaborated by KATZIN and GEBERT[14] was used.

From Fig. 3 the maximum value of D^{λ} (see Table 1 for definitions of symbols) is attained at a 1 : 1 ratio of the concentration of $CN^-/[Ni(CN)_4]^{2-}$. Data similar to

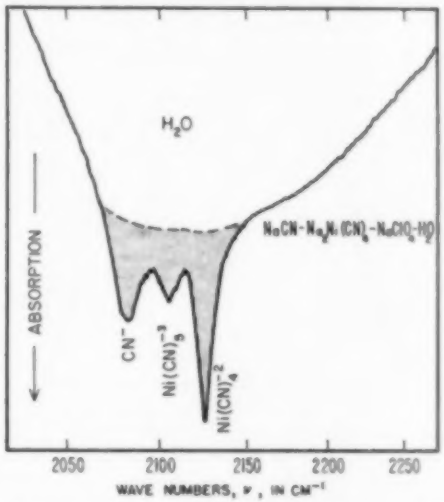

FIG. 2.—The infra-red absorption spectrum (LiF Prism) of an aqueous film (~55 × 10^{-4} cm) containing 0·085 M $[Ni(CN)_4]^{2-}$, 0·95 M CN^-, and 0·015 M $[Ni(CN)_5]^{3-}$ at ~27°. The ionic strength was maintained at 1·34 by the addition of sodium perchlorate.

that in Fig. 3 were collected from 3800 Å to 6000 Å at 100 Å intervals. In all cases the maximum value of D^{λ} was reached at a value of b_0/N consistent with the reaction

$$[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$$

Visible region. (Logarithmic treatment) An alternate method for characterization of the new species was used in the visible region.

Assume the general reaction

$$[Ni(CN)_4]^{2-} + nCN^- \leftrightharpoons [Ni(CN)_{4+n}]^{(2+n)-}$$

Since the reactant, CN^-, does not absorb in the regions of the spectra being considered, the following equations may be written: (see Table 1 for definitions of symbols)

$$[c] = K[a][b]^n \tag{1}$$

$$[a] = a_0 - [c] \tag{2}$$

$$A^{\lambda}_{obs} = [a]t\epsilon_a{}^{\lambda} + [c]t\epsilon_c{}^{\lambda}. \tag{3}$$

Appropriate substitution yields

$$\log \frac{D^{\lambda}}{[a]} = n \log [b] + \log K(\epsilon_c{}^{\lambda} - \epsilon_a{}^{\lambda}). \tag{4}$$

[13] A. JOB, *Ann. Chem.* **10**, 133 (1928).
[14] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **72**, 5455 (1950).

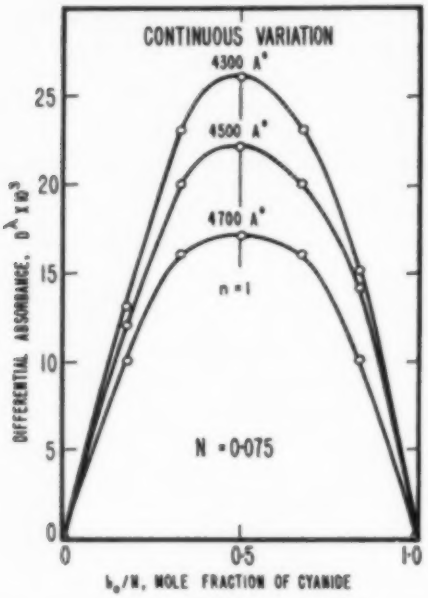

FIG. 3.—Continuous variation
Differential absorbance, D^{λ}, as a function of mole fraction of cyanide, b_0/N.

TABLE 1.—DEFINITION OF SYMBOLS

$[a]$ = the equilibrium concentration of $[Ni(CN)_4]^{2-}$, mole l^{-1}.
$[b]$ = the equilibrium concentration of CN^-, mole l^{-1}.
$[c]$ = the equilibrium concentration of $[Ni(CN)_5]^{3-}$, mole l^{-1}.
a_0 = the formal concentration of $[Ni(CN)_4]^{2-}$, mole l^{-1}.
b_0 = the formal concentration of added CN^-, mole l^{-1}.
$N = a_0 + b_0$, mole l^{-1}.
K = the concentration formation constant of $[Ni(CN)_5]^{3-}$, $\frac{[c]}{[a][b]}$, l. mole^{-1}.
ϵ_i^{λ} = the molar extinction coefficient of species i at wavelength λ, mole^{-1} l. cm^{-1}.
A_i^{λ} = the absorbance, $\log \frac{(I_0^{\lambda})}{I_i^{\lambda}}$, of species i at wavelength λ.
t = the path length of a given cell, cm.
D^{λ} = the differential absorbance, $\frac{A_{obs}^{\lambda}}{t} - a_0\epsilon_a^{\lambda}$.
A_{obs}^{λ} = the observed absorbance at wavelength λ.

If we make the approximations that

$$\log \frac{D^{\lambda}}{[a]} \cong \log \frac{D^{\lambda}}{a_0}$$

and

$$\log [b] \cong \log b_0$$

equation (4) becomes

$$\log \frac{D^{\lambda}}{a_0} \cong n \log b_0 + \log K(\epsilon_c^{\lambda} - \epsilon_a^{\lambda}). \qquad (5)$$

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If log b_0 is treated as an independent variable and log D^λ/a_0 as a dependent variable, a plot of the variables in equation (5) should yield a straight line with a slope of n and an intercept of log $K(\epsilon_c^\lambda - \epsilon_a^\lambda)$.

Fig. 4 gives a plot of the variables in equation (5). A line is drawn with a slope of one through the points of low cyanide concentration. It should be noted that the points which lie in the region of high cyanide ion concentration begin to fall away from this straight line. This is to be expected, since the approximations involved

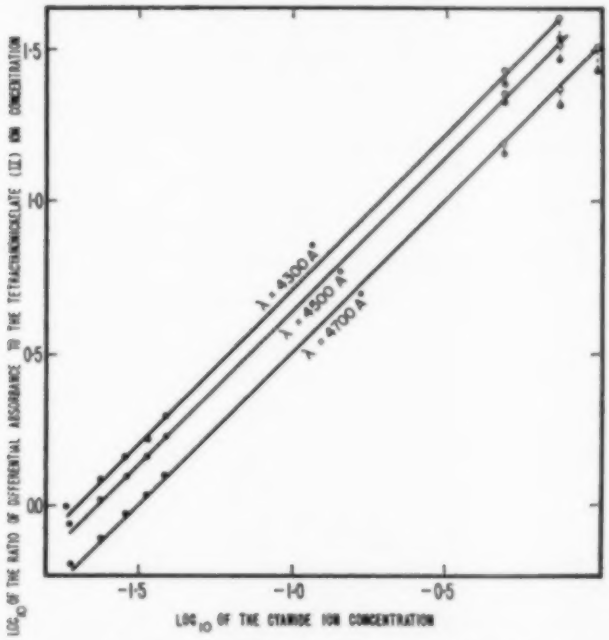

FIG. 4.—Log $(D^\lambda/a_0) = n \log b_0 + \log K(\varepsilon_c^\lambda - \varepsilon_a^\lambda)$.
A line of slope one, was constructed to pass through the points of low cyanide ion concentration. The closed circles represent the values of log D^λ/a_0 while the open circles represent the values of log D^λ/a as calculated using a value of 0·19 l. mole^{-1} for K.

in equation (5) begin to break down. The open circles in Fig. 4 represent the correction made using a value of 0·19 l./mole (see Table 4) for the formation constant. The corrected values lie nicely on a line constructed with a slope of one.

The value of $n = 1$ is consistent with the occurrence of the reaction

$$[Ni(CN)_4]^{2-} + CN^- \leftrightharpoons [Ni(CN)_5]^{3-},$$

once again showing no higher complex contributing significantly over the cyanide concentration range of 0·02–1·0 M.

The intercept, log $K(\epsilon_c^\lambda - \epsilon_a^\lambda)$, is an excellent agreement with the values determined later for K, ϵ_c^λ, ϵ_a^λ. (See Tables 3 and 4.)

Determination of the formation constant of pentacyanonickelate(II)

Visible region. Pure sodium tetracyanonickelate(II) solutions have little absorption in the visible but show rapidly increasing absorption in the ultra-violet.

The visible absorption studies, which are the subject of this section, were restricted to wavelengths greater than 4000 Å, where sodium cyanide was observed to have negligible absorption and the extinction coefficient of the tetracyanonickelate(II) ion was very low. Three wavelengths, 4700 Å, 4500 Å and 4300 Å, covering the new absorption band (see Fig. 1) were selected and the absorbance at these wavelengths was observed.

The solutions for the determination of the formation constant were divided into sets according to the ratios of the concentrations of the added cyanide to the formal tetracyanonickelate(II). Those solutions in which the added cyanide concentration is less than the formal tetracyanonickelate(II) concentration are favourable to the formation of only the next higher species (e.g. $[Ni(CN)_5]^{3-}$). Those solutions with the added cyanide concentration higher than the tetracyanonickelate(II) concentration are favourable to the formation of all higher species (e.g. $[Ni(CN_5)]^{3-}$, $[Ni(CN)_6]^{4-}$, etc.).

The equations giving the formation constant for the pentacyanonickelate(II) ion will be considered according to the ratio of the added cyanide ion concentration to the formal tetracyanonickelate(II) ion concentration, since the assumptions necessary in the derivation of the equations are dependent upon the concentration range in question.

Those solutions in which $a_0 > b_0$ will be called System I. We will assume

$$[a] \cong a_0 \tag{6}$$

$$[b] = b_0 - [c] \tag{7}$$

Therefore

$$[c] = \left[\frac{K}{1 + a_0 K}\right] a_0 b_0 \tag{8}$$

Further, the cyanide ion has no appreciable absorption in the region of the spectrum studied. By the appropriate combination and substitution of equations we arrive at the equation

$$\frac{D^\lambda}{a_0 b_0} \cong K\left[\epsilon_c{}^\lambda - \frac{D^\lambda}{b_0}\right] \tag{9}$$

(See Table 1 for definition of symbols.)

Tabulations of quantity $D^\lambda/a_0 b_0$ show (see Table 2) that for System I, $D^\lambda/a_0 b_0$ is essentially independent of the cyanide concentration, but is dependent upon the wavelength. This would imply that

$$\left[\frac{D^\lambda}{b_0} \ll \epsilon_c{}^\lambda, \epsilon_c{}^\lambda - \frac{D^\lambda}{b_0} \cong \epsilon_c{}^\lambda\right],$$

and hence that $D^\lambda/a_0 b_0 \cong \epsilon_c{}^\lambda K$ is a good approximation.

The individual values of $\epsilon_c{}^\lambda$ and K cannot be determined from the product $\epsilon_c{}^\lambda K$ for the concentrations involved in System I. However, once $\epsilon_c{}^\lambda$ is known from other data (i.e. from System II), K can be determined from this $\epsilon_c{}^\lambda K$ product.

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TABLE 2.—TYPICAL D^{λ}/a_0b_0 VALUES OF SYSTEM I AT 4700 Å AND 25·2° (t = 5 cm, μ^* = 1·34)

a_0 Tetracyanonickelate(II) concentration, (mole l^{-1})	b_0 Cyanide concentration, (mole l^{-1})	$\frac{D^{\lambda}}{a_0b_0}$
0·1000	0·02825	30·4
0·1000	0·02348	30·6
0·1000	0·01868	31·0
0·1000	0·01394	28·0
0·1000	0·00913	31·8
0·0900	0·02825	32·7
0·0900	0·02348	30·7
0·0900	0·01868	32·1
0·0900	0·01394	33·4
0·0900	0·00913	34·0
0·0800	0·03783	33·4
0·0800	0·03304	32·6
0·0800	0·02825	32·8
0·0800	0·02348	33·0
0·0800	0·01868	34·8
0·0700	0·03783	31·3
0·0700	0·03304	31·6
0·0700	0·02825	31·9
0·0700	0·02348	31·6
0·0700	0·01868	32·9
0·0600	0·03783	34·3
0·0600	0·03304	32·8
0·0600	0·02825	33·1
0·0600	0·02348	34·8
0·0600	0·01868	36·6

Average = 32·5 ± 1·8

* Ionic strength maintained by the addition of sodium perchlorate.

Those solutions in which $b_0 > a_0$ will be called System II. We will assume

$$[b] \cong b_0 \tag{10}$$

$$[a] = a_0 - [c] \tag{11}$$

therefore

$$[c] = \left[\frac{K}{1 + b_0K}\right] a_0b_0 \tag{12}$$

By the appropriate combination and substitution of equations we arrive at an equation similar to the one obtained by MCCONNELL and DAVIDSON[15]

$$\frac{a_0b_0}{D^{\lambda}} = \frac{b_0}{(\epsilon_c^{\lambda} - \epsilon_a^{\lambda})} + \frac{1}{K(\epsilon_c^{\lambda} - \epsilon_a^{\lambda})}. \tag{13}$$

[15] H. MCCONNELL and N. DAVIDSON, *J. Amer. Chem. Soc.* **72**, 3164 (1950).

If b_0 is treated as an independent variable and a_0b_0/D^λ as a dependent variable, then equation (13) is an equation of a straight line with slope $(1/\epsilon_c{}^\lambda - \epsilon_a{}^\lambda)$ and intercept $1/K(\epsilon_c{}^\lambda - \epsilon_a{}^\lambda)$. Table 3 gives typical data for System II.

The values for $\epsilon_a{}^\lambda$ were determined independently (see Table 5). By performing the standard linear regression analysis on the data of System II, the values of K, $\epsilon_c{}^\lambda$, and their respective standard deviations were obtained (see Tables 4 and 5).

TABLE 3.—TYPICAL VARIABLES OF SYSTEM II AT 4700 Å AND 25·2° FOR THE EQUATION

$$\frac{a_0b_0}{D^\lambda} = \frac{b_0}{(\epsilon_c{}^\lambda - \epsilon_a{}^\lambda)} + \frac{1}{K(\epsilon_c{}^\lambda - \epsilon_a{}^\lambda)} \quad (t = 1 \text{ cm}, \mu^* = 1{\cdot}34)$$

a_0 Tetracyanonickelate(II) concentration (mole l^{-1})	b_0 Cyanide concentration, (mole l^{-1})	$\frac{a_0b_0}{D^\lambda}$
0·1000	0·9653	0·03563
0·0900	0·9653	0·03640
0·0800	0·9653	0·03650
0·0700	0·9653	0·03663
0·0600	0·9653	0·03582
0·1000	0·7233	0·03581
0·0900	0·7233	0·03617
0·0700	0·7233	0·03450
0·0600	0·7233	0·03449
0·1000	0·4816	0·03393
0·0900	0·4816	0·03349
0·0800	0·4816	0·03375
0·0700	0·4816	0·03307
0·0600	0·4816	0·03316

* The ionic strength was maintained by the addition of sodium perchlorate.

Using the value of $\epsilon_c{}^\lambda$ and its standard deviation it was then possible to determine K from System I. A comparison between the values of K so obtained for System I and System II is given in Table 4.

It should be emphasized again that the concentrations in System I are favourable to the formation of *lower* complex species in the solution, while the concentrations in System II are favourable to the formation of *higher* complex species. The excellent correlation between the K values in Table 4 once again indicates the existence of only one new species appearing in the concentration range studied, namely $[Ni(CN)_5]^{3-}$.

Infra-red region. (Moderate cyanide concentrations.) In the infra-red region, distinct peaks were observed corresponding to each of the species in solution (see Fig. 2). Since the molar extinction coefficient for the tetracyanonickelate(II) ion can be determined independently (see Table 5) and the path length is known, the equilibrium concentration of tetracyanonickelate(II) may be calculated. The concentration of the pentacyanonickelate(II) will then be the difference between the initial and

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TABLE 4.—VALUES OF K AT 25·2° FOR THE EQUILIBRIUM: $[Ni(CN)_4]^{2-} + CN^- \leftrightharpoons [Ni(CN)_5]^{3-}$ ($\mu = 1{\cdot}34$)

λ (Å)	$K \pm S_K$	
	System I	System II
4300	0·19 ± 0·04	0·20 ± 0·04
4500	0·21 ± 0·04	0·21 ± 0·03
4700	0·18 ± 0·03	0·18 ± 0·02

$K = 0{\cdot}19 \pm 0{\cdot}01$ l. mole^{-1}

(This value of K was determined from 39 different solutions, each measured at the three wavelengths given above.)

TABLE 5.—INFRA-RED ABSORPTION FREQUENCIES OF AQUEOUS CYANIDE SPECIES AND THEIR MOLAR EXTINCTION COEFFICIENTS

Species	ν (cm^{-1})	ϵ (moles^{-1} l. cm^{-1})
CN^- [1]	2080 ± 2	29 ± 1
$[Ni(CN)_5]^{3-}$	2102 ± 2	1730 ± 230
$[Ni(CN)_4]^{2-}$	2124 ± 1	1068 ± 95

THE MOLAR EXTINCTION COEFFICIENT OF AQUEOUS CYANIDE SPECIES IN THE VISIBLE REGION

λ (Å)	ϵ (mole^{-1} l. cm^{-1})		
	CN^-	$[Ni(CN)_4]^{2-}$	$[Ni(CN)_5]^{3-}$
4300	0	1·811 ± 0·005	263 ± 59
4500	0	1·350 ± 0·008	213 ± 38
4700	0	0·967 ± 0·009	178 ± 25

equilibrium concentration of tetracyanonickelate(II). The equilibrium concentration of cyanide is given by the difference between the initial cyanide concentration and the concentration of the pentacyanonickelate(II). The average value of K, obtained in the infra-red region, for fourteen of the same solutions (System II) which had been used in the visible region was $0{\cdot}3 \pm 0{\cdot}1$ l. mole^{-1}.

The K values determined from the infra-red absorption data are less accurately known than the K values determined from the visible absorption data. The large standard deviation arises from the large percentage errors in background corrections and the uncertainty in peak overlap. Nevertheless, the K values from the infra-red data are in substantial agreement with the K values obtained in the visible region.

Infra-red region. (High Cyanide Concentrations). The value of K, determined for very concentrated cyanide solutions (5 M cyanide and 0·4 M tetracyanonickelate(II)) was found to be 0·4 l./mole, μ = ca. 6.

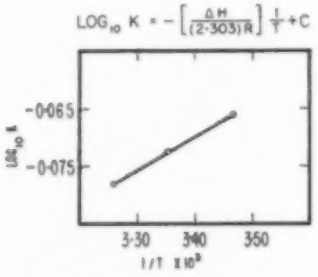

FIG. 5.—Log K as a function of $1/T$.

Once again the value of the constant is in substantial agreement with the values of K obtained in the visible region.

It should be emphasized that even at these very high cyanide to tetracyanonickelate(II) *concentration ratios, no new absorption,* other than the peak corresponding to $[Ni(CN)_5]^{3-}$, was ever observed in the infra-red region.

The determined average value of K (Table 4) justifies the assumptions employed in this and the preceding sections.

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Determination of ΔH

By the use of equations (9) and (13), K was found to be 0·22 $\pm$ 0·01, 0·19 $\pm$ 0·01 and 0·17 $\pm$ 0·01 for the temperatures 15·4°, 25·2° and 33·6°, respectively.

Fig. 5 gives log K as a function of $1/T$ for the temperature interval of 15°–35°. A ΔH of ~ -3kcal/mole is consistent with the slope of the line in Fig. 5.

Determination of the magnetic susceptibility of the pentacyanonickelate(II) *ion*

The magnetic susceptibility of pentacyanonickelate(II) ion was determined by the Gouy method of observing the apparent change in weight of a solution in a magnetic field. A change in apparent weight of 0·0111 g for 10 ml of a solution containing $\sim$0·3 M $[Ni(CN)_5]^{3-}$, $\sim$0·1 M $[Ni(CN)_4]^{2-}$, and $\sim$4·5 M CN^- was observed. The apparent changes in weight of pure solutions of $[Ni(CN)_4]^{2-}$ and of CN^- were observed separately and appropriate corrections were made for the solution containing the mixture of the species. The results showed that $[Ni(CN)_5]^{3-}$ was diamagnetic. As an indication of the sensitivity of the apparatus, a dilute solution ($\sim$0·01 M) of $[Fe(CN)_6]^{3-}$ was observed, and was shown to be in agreement with the known paramagnetic susceptibility of $[Fe(CN)_6]^{3-}$.

Possible structure of the pentacyanonickelate(II) *ion*

The preceding sections show conclusively that the predominant new species in aqueous solutions of tetracyanonickelate(II) and cyanide ion is the pentacyanonickelate(II) ion. Whether the existence of an odd number of cyanide ligands truly implies an odd co-ordination number, or whether an aquo complex is involved has not been shown. However, of special interest to this work is the report by ADAMSON[16] that the ion $[Co(CN)_5]^{3-}$ is the true species in aqueous solution rather than $[Co(CN)_5]\cdot H_2O^{3-}$ as reported by HUME and KOLTHOFF[17].

In either case, i.e. $[Ni(CN)_5]^{3-}H_2O$ or $[Ni(CN)_5]^{3-}$, the ligand field theory would allow a diamagnetic complex, in which the cyanide ligands are arranged in a tetragonal pyramide around the nickel(II) atom.

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A STUDY OF TRANSFERENCE AND SOLVATION PHENOMENA—I

URANYL CHLORIDE IN WATER, ETHANOL AND WATER–ETHANOL SOLVENTS*

D. M. MATHEWS, J. O. WEAR and E. S. AMIS
Chemistry Department, University of Arkansas, Fayetteville, Arkansas

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Abstract—Transference and solvation phenomena involving uranyl chloride (UO_2Cl_2) have been studied at 25·00 ± 0·01°C in water, ethanol and water–ethanol solvents. Transference phenomena as a function of the concentration of UO_2Cl_2 have been studied at the same temperature in water and in 99·7 weight per cent ethanol in water. The transference number of the anion in both water and in 99·7 weight per cent ethanol extrapolates to 0·64 and the cation to 0·36 at infinite dilution of the UO_2Cl_2. The transference number of the anion as a function of concentration reaches a maximum of unity at about 19·5 weight per cent UO_2Cl_2 and then decreases sharply with further increase of salt concentration. The maximum in water is explained as possibly arising from $[UO_2Cl_2 \cdot solvent]^-$ and $[UO_2Cl \cdot solvent]^+$ ions of equal mobility. The dependence of anion transference number on solvent composition is qualitatively in agreement with the dependence, with respect to uranium (VI) ion, of the order of the electron exchange reaction between uranium (VI) and uranium (IV) ions. The plot of the moles of water per faraday transported from anode to cathode gave a sine-like curve when plotted against weight per cent ethanol in the solvent. The shape of this curve was explained on the basis of the alternate removal of layers of water of hydration on the $UO_2Cl_2^-$ and UO_2Cl^+ ions and the successive replacement of these hydration layers with ethanol.

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IN our conductance work[1–5] and in our studies of rates of electron exchange reactions[6,7,8] in pure and mixed solvents, we have found the need of knowing something more of the nature of the ions in solution and of the nature and extent of solvation of these ions. It was felt that studies of the conductance and transference number of electrolytes in mixed solvents might help in the determination of the nature of the ions and the nature and extent of their solvation in pure and mixed solvents. This is a report of the studies of the transference numbers of the ions of uranyl chloride in water, in ethanol containing slight amounts of water and in water–ethanol mixtures of various compositions.

EXPERIMENTAL

Preparation of uranyl chloride monohydrate was carried out as described by HEFLEY *et al.*[9] In the case of water as solvent, about 50 g of fructose, the amount of uranyl chloride necessary to give

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the desired concentration and about 400 ml of distilled water were stirred until the solids were completely dissolved. This solution was transferred to a 1 l. volumetric flask and diluted to the mark with distilled water.

A vibration-free support which was used to suspend the transference cell was secured to a sturdy wall-shelf external to the water bath. During electrolysis, care was taken not to disturb the shelf to which the support rods were connected since this would agitate the solution in the transference cell.

The water in the constant temperature bath was stirred with a cone-drive stirrer set at low speed. Since the only vibrations that could encounter the transference cell were through the water, the slow stirring rate served to minimize them.

The silver chloride electrode was prepared by electrolysing a number 20 B and S gauge silver wire in a 1 M solution of lithium chloride using a silver chloride cathode. Ten times as much current was passed through this solution as would be passed through a solution used in a transference determination. Before use, the electrode was washed three times with distilled water and three times with the solution to be used in the transference number determination.

After realizing that the silver chloride cathode would always liberate some hydrogen in uranyl chloride solution, probably due to the hydrolysis of the uranyl chloride to produce hydrochloric acid and the subsequent electrolysis of the hydrogen ion, this side of the transference cell was fitted with an 8 mm glass tube through which the evolved hydrogen could escape. Since this was the only opening in the cell, the solution did not rise above the desired point in this tube. This tube also served as an entrance for the copper wire which was connected to the silver chloride cathode. Since the electrode reaction was not known exactly in the cathode compartment, only the anode compartment was used with the middle for the analyses and calculations.

The silver anode in the transference apparatus was a spiral of number 20 B and S gauge silver wire. It was etched in hot nitric acid and washed in the same manner as the silver chloride cathode before use.

The clean, dry cell was filled with the solution to be used, emptied into a beaker with the remainder of the solution, refilled and thermostated at 25·00°C prior to starting the current flow.

There were two silver coulometers in the electric circuit, one before and one after the transference cell. Thus, any current leak in the cell could be detected. In each coulometer a weighed platinum dish served as a cathode. The platinum dish was filled approximately half-way with a 1 M solution of silver nitrate. A porous cup, supported by a lucite stand, was placed in the solution and around the silver anode to catch anode slag. These silver coulometers were used in the usual way to obtain the number of faradays.

A constant voltage was maintained by means of a Sargent constant voltage supply ($\pm$0·5 per cent from 0 to 100 mA) in conjunction with a Sola constant voltage transformer ($\pm$1·0 per cent).

Whenever possible, current was passed through the solution at the rate of 20–30 mA for sufficient time to give about 0·01 faraday of electricity. In solvents containing high weight per cents of alcohol, the resistance of the solution was too great to obtain 20–30 mA and currents of 10 mA minimum were passed for a longer time. The water bath was maintained at 25·00 $\pm$ 0·01°C. The thermometers were calibrated against a National Bureau of Standards calibrated thermometer.

When the current had passed through the system for a sufficient length of time, or when the current had to be stopped for other reasons (e.g. gas bubbles around an electrode), the stopcocks of the transference cell were turned in such a manner as to isolate the various cell compartments. The solutions in the middle and anode compartments were transferred to ground-glass-stoppered erlenmeyer flasks. The erlenmeyer flask to which the anode compartment solution was added was previously tared. The film of solution adhering to the walls of the anode compartment was quantitatively washed into a 400 ml beaker and the total chloride content determined. From this total chloride and the grammes of chloride per gramme of undiluted solution in the anode compartment the weight of the film of solution that adhered to the walls of the anode compartment could be calculated. Thus, after weighing the anode solution and flask, the total weight of the anode solution was obtained.

Portions of the solutions from the transference cell were placed in clean dry weight burettes and weighed samples taken for analysis. After proving that the uranyl to chloride ratio remained 1 : 2, only chloride analyses were used. Three portions each of the original solution, middle compartment and anode compartment were taken for analysis. In event that the original solution and the solution

from the middle compartment gave different concentration, the transference determination was abandoned. The difference in concentration between the middle and anode compartment solutions was used along with the total weight of solution in the anode compartment and the weight of silver deposited in the coulometers to determine the apparent transference number.

The degree of rotation of each of the three separate solutions for water solvent was measured using a Rudolph Model 80 high precision polarimeter. The polarimeter tube was water-jacketed and 400 mm in length. A constant temperature was maintained at 25·00 ± 0·01°C by pumping water from the bath described above through the jacket of the polarimeter tube. The polarimeter tube and the cover glasses that sealed its ends were cleaned before use, and the tube was rinsed three times before use with the solution whose optical rotation was to be measured. A sodium lamp was used as a light source for the polarimeter.

The measurements of rotation were always made in a dark room. The tube was filled, the room darkened, and the operator remained in the dark for 30 min. The first three to five readings were always discarded since the eyes would over-adjust and the first measurements were nearly always spurious. Ten measurements were made on a given solution and the average deviation from the average calculated. If the deviation was greater than 0·004 circular degrees, the readings were discarded and the measurements repeated.

From the data described to this point, it was possible for water solvent to calculate the moles of water transferred in a given direction per faraday. An equation was derived for use in the calculations starting with the equation:

$$g = \frac{100\alpha}{\lambda[\alpha]_{sp}\, d}$$

where g is the grams of fructose per 100 g of solution; α the absolute value of the measured rotation; $[\alpha]_{sp}$ the specific rotation of the reference material, fructose; d the density of the solution; and λ expresses the length of the polarimeter tube which in this case was 40 cm.

The difference in concentration of sugar is given by $g_m - g_a$, where the subscripts a and m refer to the anode and middle compartments, respectively. A positive value of $g_m - g_a$ indicates that water is transferred into the cathode compartment. From the above relation

$$g_m - g_a = \frac{100\alpha_m}{4[\alpha]_{sp}\, d_m} - \frac{100\alpha_a}{4[\alpha]_{sp}\, d_a}.$$

Since the salt content in the middle compartment may be different from the salt content in the anode compartment, the angles of rotation are compared by extrapolating to equal salt concentrations. That is, the per cent sugar in 100 g of solution rediluted with the correct ratio of solvent and sugar to a total of 100 g after the removal by transference of a quantity of salt is less if there is less salt present, since the weight of salt enters into the total weight of solution. Thus, if a solution contains g grams of sugar in a 10 per cent salt solution, it contains g/0·90 g of sugar per 100 g of solution, exclusive of the salt. The anode compartment had become enriched in sugar compared to the middle compartment due to loss of salt from the anode region. When compared at a zero salt concentration

$$g_m' - g_a' = \frac{100\alpha_m}{4[\alpha]_{sp}\, d_m(1 - f_s^m)} - \frac{100\alpha_a}{4[\alpha]_{sp}\, d_a(1 - f_s^a)} \tag{1}$$

$$g_m' - g_a' = \frac{K\alpha_m}{d_m(1 - f_s^m)} - \frac{K\alpha_a}{d_a(1 - f_s^a)} \tag{2}$$

where f is the fraction that the salt is of the solution and K is the combined value of the constants in the terms on the right of the equality sign in equation (1). The g' values in equations (1) and (2) represent the grammes of sugar per 100 g of solution other than salt. When the rotations are compared at the same salt per cent (p_m) this becomes:

$$g_m'' - g_a'' = \frac{K\alpha_m(1 - f_s^a)}{d_m(1 - f_s^m)} - \frac{K\alpha_a}{d_a} \tag{3}$$

Now

$$\frac{1 - f_s^a}{1 - f_s^m} = 1 + \frac{f_s^m - f_s^a}{1 - f_s^m}$$

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which expressed as per cent becomes

$$1 + \frac{p_s^m - p_s^a}{100 - p_s^m},$$

and substituting into equation (3) gives:

$$g_m'' - g_a'' = \frac{100}{4[\alpha]_{sp}} \left[\frac{\alpha_m}{d_m} \left(1 + \frac{p_s^m - p_s^a}{100 - p_s^m} \right) - \frac{\alpha_a}{d_a} \right] \tag{4}$$

This equation gives the change in grammes of optically active reference material per hundred grammes of solution and multiplying by (W/100), the weight of the anode compartment in hundreds of grammes, gives the total difference in weight of sugar between the middle and anode compartments. This change in grammes of sugar divided by the weight of sugar per gramme of solution gives the grammes of solution necessary to contain this weight of sugar, and this is the weight of solution that must be replaced by water in order to cause the measured difference in sugar concentration. The weight of sugar per gramme of solution is:

$$g_m = \frac{\alpha_m}{4[\alpha]_{sp}\, d_m},$$

and the grammes of water transferred are:

$$g_{H_2O} = \frac{\left[\alpha_m \left(1 + \frac{p_s^m - p_s^a}{100 - p_s^m} \right) - \alpha_a \frac{d_m}{d_a} \right] W}{\alpha_m} \tag{5}$$

and the moles of water transported per faraday are:

$$\Delta N_{H_2O}^F = \frac{\left[\alpha_m \left(1 + \frac{p_s^m - p_s^a}{100 - p_s^m} \right) - \alpha_a \frac{d_m}{d_a} \right] W}{18\, F \alpha_m} \tag{6}$$

It has been assumed in this derivation that the density of the water that replaces the solution is the same as the density of the solution. With the help of this equation, the data in the following pages were used to calculate the number of moles of water transported per faraday when the solvent was water.

Procedure in ethanol and water–ethanol solvents

The procedure was considerably different in these solvents from that in water since there is a reaction between ethanol and fructose with the probable formation of a hemiketal or ketal and the consequent lowering of the optical rotation eventually to zero. Moreover, the rotation change is different in the different compartments. This could be caused by catalysis of the ethanol–fructose reaction by a particular electrode. The silver chloride electrode does not function normally in ethanol, but instead there is a removal of hydrogen and thus the properties of the cathode solutions are not comparable to the same solutions in water solvent.

To overcome this difficulty, an attempt was made to prepare ethyl D-fructofuranoside in a manner similar to the PURVES and HUDSON preparation of the methyl derivative.[10] Using this procedure, the yield was so low that purification was not attempted.

Because of the time needed to obtain a different reference substance, the transference number determinations were continued using only the water and ethanol in the solvent as a reference.

It was necessary to prepare the uranyl chloride solutions in these solvents immediately before use because of the slow decomposition which occurs. The solutions were prepared as in water with the exception that the fructose was left out, and the determinations of apparent transference numbers were also the same as described for water.

In order to gain information concerning solvations of ions, each compartment was analysed for per cent ethanol. The analyses were performed by use of a standard table of density as a function of the per cent ethanol in water–ethanol mixtures. The densities of the standard table were precise to within ±0·000002 g/ml, but in the procedure to be used for analyses, the precision dropped to ±0·00002 g/ml.

[10] C. B. PURVES and C. S. HUDSON, *J. Amer. Chem. Soc.* **56**, 708 (1934).

In order to analyse the individual compartments for solvent composition, it was first necessary to separate the solute and solvent. Moreover, since HCl was formed from hydrolysis, it had to be neutralized or it would have distilled over with the solvent.

The procedure was to place a weighed amount of a compartment solution into the 500 ml pot of a vacuum distillation apparatus. A 4 M solution of sodium hydroxide, sufficient to neutralize the HCl and precipitate the uranium as sodium uranate, was added through a side arm equipped with a high vacuum stopcock. The distilling apparatus was assembled and the mixture in the pot frozen in a dry-ice–toluene mixture. After freezing, the apparatus was evacuated with a Welch Duo Seal vacuum pump and isolated by closing the high vacuum stopcock near the receivers. The pot was then removed from the cold bath and the receiver cooled in the same bath. The pot was warmed from above with a heat lamp to prevent bumping and the distilling head possessed shelf-like indentations on alternating sides to prevent solid from being carried over. When the pot had boiled nearly dry, 20 ml of distilled water were added through the side arm without releasing the vacuum and the distillation continued until the pot was dry. The apparatus was then heated gently to insure that all of the alcohol was in the receiver.

The previously weighed receiver was stoppered, washed, allowed to dry in the room and reweighed. Two 20 ml Sprengel-type pycnometers were filled with a portion of this solution and its density measured at 25·00°C. From the density vs. composition plot, the per cent alcohol in the solution could be determined. The total weight of the alcohol present could thus be determined and consequently, the per cent alcohol in the solution being investigated obtained.

The calibrated arms of the Sprengel-type pycnometers were standardized with mercury and the liquid level was read with a telescope at a distance of 3 ft from the pycnometer. Special care was taken to avoid parallax and all readings were taken with the pycnometer in the same position and the trademark toward the reader. All weights were corrected to vacuum.

Since transference numbers are based on a given weight of solvent the per cent ethanol was calculated on the basis of a definite solute concentration equal to the concentration in the anode compartment.

The grammes of ethanol that are in excess in the middle compartment or the loss in the anode compartment is given by the relation

$$\left(\frac{p_e^m - p_e^a}{100}\right) W,$$

where p_e^m and p_e^a are the per cents ethanol in the middle and anode compartments, respectively.

Since there are $p_e^m/100$ g of ethanol per gramme of solution, the grammes of solution displaced by water or ethanol are:

$$\left(\frac{p_e^m - p_e^a}{100}\right) W \left(\frac{100}{p_e^m}\right) \quad \text{or} \quad \left(\frac{p_e^m - p_e^a}{p_e^m}\right) W,$$

where W is taken as the weight of solvent. The moles of water transported per faraday ($\Delta N_W{}^F$) are then

$$\Delta N_W{}^F = \left(\frac{p_e^m - p_e^a}{18\,F p_e^m}\right) W = \frac{1}{18F}\left(1 - \frac{p_e^a}{p_e^m}\right) W$$

It should be mentioned that it is assumed in these equations that the density of the solvent in the solution is the same as the density of the solution.

DATA

The symbols in the following tables have the meanings listed below:

α = angular rotation of the plane of polarization by the solution at 25°C.
Ag = grammes of silver deposited in the coulometer.
W = total mass in grammes of the electrode portion.
W_s = total mass in grammes of solvent in the electrode portion.
F = equivalents of electricity passed through the solution.
T^c, T^a = Hittorf transference number of cation and anion, respectively.

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ΔN_W^F = number of moles of water transferred from anode to cathode per faraday of electricity.
ΔN_E^F = moles of ethanol transferred from cathode to anode per faraday.
p_s = per cent of electrolyte in the solution.
p_e = per cent of ethanol in the solution.
p_r = per cent of fructose in the solution.
d_a^a, d^m = density of anode and middle portion, respectively.
d_d^a, d_d^m = density of distillate from the respective portions.
w_{ss}^a, w_{ss}^m = weight of solvent in the respective portions.
w_d^a, w_d^m = weight of distillate from samples.
p_{ed}^a, p_{ed}^m = per cent ethanol in the distillate from the respective portions.
p_{es}^a, p_{es}^m = per cent ethanol in the solvent from the respective samples.
N^a, N^m = moles electrolyte per gramme of solution in the respective samples.
p_e^m = per cent ethanol in middle compartment sample.

The data needed for calculation of transference and solvation numbers in water solutions are given in Table 1. The density data for 23·3980 weight per cent solution

TABLE 1.—WATER SOLVENT DATA

Conc. (wt. %)	1·8055	1·8055	5·3000	19·7192	19·7205	23·3980
α_a	21·333	21·334	22·780	24·232	24·227	
α_m	21·324	21·322	22·770	24·218	24·214	
Ag	0·71749	0·5843	0·88109	0·24432	0·27432	0·17150
Ag_2	0·71744	0·5869	0·88130	0·27432	0·27432	0·17142
p_s^a	1·5201	1·5752	4·9681	19·7192	19·7205	23·3633
p_s^m	1·8055	1·8055	5·3000	19·7192	19·7205	23·9800
W	136·937	138·38	117·347	142·423	158·50	166·194
ΔN_s	$2·2923 \times 10^{-3}$	$1·8693 \times 10^{-3}$	$2·284 \times 10^{-3}$	0	0	$3·383 \times 10^{-4}$
F	$6·6506 \times 10^{-3}$	$5·428 \times 10^{-3}$	$8·1683 \times 10^{-3}$	$2·543 \times 10^{-3}$	$2·543 \times 10^{-3}$	$1·5894 \times 10^{-3}$
T^a	0·655	0·655	0·720	1	1	0·787
T^c	0·345	0·345	0·280	0	0	0·213
$1 + K$	1·002894	1·002342	1·00350	1	1	
$\alpha_m(1 + K)$	21·385	21·372	22·850	24·218	24·214	
d_m/d_a	1·0013	1·0010	1·0029	1	1	
$\alpha_a(d_m/d_a)$	21·361	21·355	22·846	24·232	24·227	
$18F_m$	2·5526	2·0832	3·3479	1·1086	1·1084	
ΔN_W^F	−1·29	−1·13	−0·14	1·80	1·86	

were not taken and therefore the ΔN_W^F could not be calculated. The plot in Fig. 1 shows the dependence of transference number on concentrations, and from this plot the transference number of the anion would extrapolate to about 0·64 at zero salt concentration. This would give a transference number for the cation of 0·36. These are not unreasonable values for transference numbers of the two ions at infinite dilution. The transference number of the anion at first increases with salt concentration and, within the limits of our experimental data, reaches a maximum at about 19·5% UO_2Cl_2 and then decreases sharply with further increase of salt concentration. This indicates complex ion formation at high UO_2Cl_2 concentration. The ions probably involve the uranyl in a negative complex. For example, if an ion, $[UO_2Cl_2 \cdot solvent]^-$, had the same mobility as a $[UO_2Cl \cdot solvent]^+$ ion but was traveling in an opposite direction, the only apparent transfer would be that of chloride ions. This would explain the observed maximum in the transference number versus weight per cent UO_2Cl_2 curve. To explain the drop beyond the maximum, further complex formation would have to be postulated.

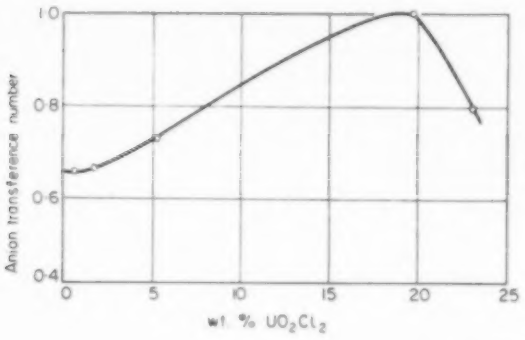

FIG. 1.—Anion transference number of uranyl chloride in water solution plotted against concentration.

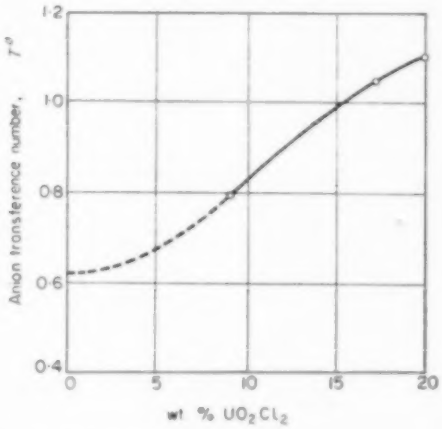

FIG. 2.—Anion transference number plotted against concentration for UO_2Cl_2 in 99·7 per cent ethanol.

TABLE 2.—TRANSFERENCE NUMBERS OF $UO_2Cl_2 \cdot H_2O$ IN 99·7 PER CENT ETHANOL

Conc. (wt. %)	9·1406	19·9226	17·049
Ag	0·96155	0·72035	0·27625
Ag_s	0·96137	0·71986	0·27661
p_s^a	8·8682	20·0177	17·0608
p_s^m	9·1406	19·9226	17·049
W	116·05	115·099	157·355
ΔN_s	$1·854 \times 10^{-3}$	$-6·423 \times 10^{-4}$	$-1·0891 \times 10^{-4}$
F	$8·9123 \times 10^{-3}$	$6·675 \times 10^{-3}$	$2·5621 \times 10^{-3}$
T^a	0·792	1·096	1·043
T^c	0·208	−0·096	0·043

The data from the measurement of transference numbers of uranyl chloride monohydrate in 99·7 per cent ethanol solution are listed in Table 2. A plot of transference numbers against concentration can be seen in Fig. 2.

In Table 3 are recorded the data taken on KCl. These data were taken as a check of procedure and the KCl data agree well with data recorded in the literature.[11]

In Table 4 are recorded transference and solvation data of solutions of uranyl

[11] E. W. WASHBURN and E. B. MILLARD, *J. Amer. Chem. Soc.* **37**, 694 (1915).

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TABLE 3.—TRANSFERENCE AND SOLVATION DATA ON KCl IN WATER

Solute	KCl
Conc. (wt. %)	7·0248
α_a	19·209
α_m	19·199
Ag_1	0·21079
Ag_2	0·21075
p_s^a	6·9531
p_s^m	7·0248
W	99·001
ΔN_s	$9·521 \times 10^{-4}$
F	$1·9539 \times 10^{-5}$
T^a	0·512
T^c	0·488
$(1 + K)$	1·0007712
$\alpha_m(1 + K)$	19·214
d_m/d_a	1·00048
$\alpha_a(d_m/d_a)$	19·218
$18F_m$	0·67523
ΔN_W^F	0·586
H_3O/K^+	4·81

TABLE 4.—TRANSFERENCE AND SOLVATION DATA ON UO_2Cl_2 IN ETHANOL–WATER SOLVENTS

d_d^a	0·972424	0·97604	0·986742	0·972051	0·980324	
d_d^m	0·972779	0·979522	0·988502	0·974594	0·972760	
W_{ss}^a	42·4915	34·2740	30·1806	20·5409	15·5965	
W_{ss}^m	37·0791	30·1642	34·5477	18·5495	20·6163	
p_s^a	15·0654	25·8853	9·7662	11·75086	8·9001	11·74747
p_s^m	15·3280	26·1308	10·2388	12·21121	9·3502	12·17711
W_d^a	148·1952	139·5270	85·4082	109·7284	128·8585	
W_d^m	128·5760	147·6121	119·7379	111·9130	116·4511	
p_{cd}^a	15·73214	13·25799	6·50167	15·99937	10·57355	
p_{cd}^m	15·47206	11·08003	5·40159	14·19823	15·49141	
p_{cs}^a	53·60656	53·96977	18·39923	85·46826	86·07636	87·15545
p_{cs}^m	53·65124	54·22156	18·56476	85·66106	87·50309	85·2933
$N^a \times 10^4$	4·418	7·591	2·864	3·446	2·610	3·445
$N^m \times 10^4$	4·495	7·663	3·003	3·581	2·742	3·571
W	137·7959	153·7010	121·2407	121·2639	129·8753	121·1458
W_s	117·0364	113·5377	109·4001	107·0144	118·3163	
$F \times 10^2$	9·0934	11·08	13·1763	12·128	10·4290	12·3367
$p_{ss}^m - p_{ss}^a$	0·04468	0·2519	0·1655	0·1928	0·4153	
p_s^m	45·4722	42·988	16·762	76·3391	80·0210	
ΔN_W^F	0·703	3·34	4·55	1·24	3·27	
ΔN_E^F	0·275	1·31	1·78	0·484	1·28	
T^c	0·233	0·199	0·256	0·270	0·329	0·247
T^a	0·767	0·801	0·744	0·730	0·671	0·753

chloride in ethanol–water solvent mixtures. Fig. 3 is a plot of anion transference number vs. weight per cent ethanol in the solvent at a uranyl chloride concentration of 10·24 weight per cent.

In Fig. 3 and Table 4 the anion transference number is seen to decrease at first with increasing weight per cent alcohol, then remain constant from about 19 to 54 weight per cent alcohol and reach a minimum at about 81 per cent ethanol, after

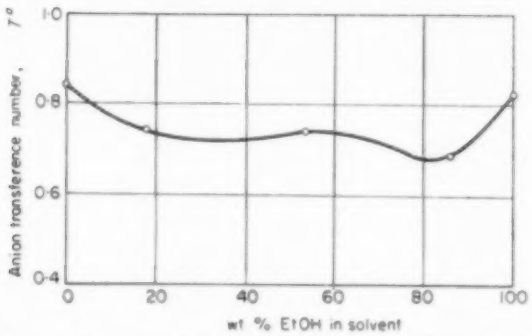

FIG. 3.—Anion transference number vs. per cent ethanol in solvent at 10·24 wt. % UO_2Cl_2.

which it again increases up to 100 per cent ethanol. Except for the decrease of the anion transference number with the first small additions of alcohol, the shape of the anion transference number vs. composition of solvent curve is quite similar to the order of the uranium (VI) ion vs. solvent composition curve for the electron exchange reaction between uranium (VI) ion and uranium (IV) ion in the presence of hydrochloric acid.[8] The decrease from the constant portions of the curves and the minima of the two curves occur at about the same alcohol compositions of the solvent. These correlations are striking and perhaps indicate the influence of similar ion complexes on the transference and kinetic phenomena. The striking dependence of both of these phenomena on solvent composition would imply that the uranyl ion species vary with the percentage of alcohol in the solvent over certain ranges of composition.

Table 4 also records the moles of water transferred from anode to cathode per faraday of current and the moles of ethanol transferred from cathode to anode per faraday of current in solvents of different alcohol compositions and in different concentrations of uranyl chloride.

Table 5 records the values of density of uranyl chloride solution in water solvent at various concentrations. These data were used in calculating solvation numbers.

Fig. 4 shows that the moles of water transported per faraday from the anode to the cathode compartment in water solvent increase from −1·8 at zero wt. % UO_2Cl_2 to 1·8 at about 20 wt. % UO_2Cl_2. This implies that in dilute solutions, the anion is transporting more water than the cation, whereas in more concentrated solutions, the cation is carrying more water than the anion. This last statement harmonizes with our reasoning concerning the mobility of the $UO_2Cl_3^-$ and the UO_2Cl^+ ion at around 20 wt. % UO_2Cl_2. The $UO_2Cl_3^-$ ion being larger than the UO_2Cl^+ ion would tend to offer more resistance to motion through the solution if unsolvated than the UO_2Cl^+ ion if unsolvated. However, if the UO_2Cl^+ were more highly solvated, then the mobilities of the two ions conceivably could be equal. On the basis of this reasoning, the anion

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TABLE 5.—DENSITIES OF UO_2Cl_2 SOLUTIONS OF VARIOUS CONCENTRATIONS IN WATER

UO_2Cl_2 (%)	Moles/1000 g solution	Density
14·6519	0·4297	1·13414
13·1243	0·3849	1·11820
7·3277	0·2149	1·06140
4·6169	0·1354	1·03671
2·5018	0·07337	1·01071
0·69080	0·02026	1·002696
0·36103	0·01059	1·000061

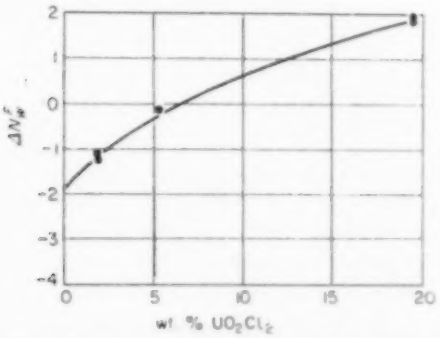

FIG. 4.—Moles of water transported from anode to cathode compartment per F of electricity plotted against weight per cent uranyl chloride in the solution.

having a transference number of greater than one at 20 wt. % UO_2Cl_2 in 99·7 per cent ethanol is relatively less solvated compared to the cation in the alcoholic solution than in pure water. The plot of the anion transference number vs. wt. % UO_2Cl_2 in 99·7 weight per cent ethanol shown in Fig. 2 strikingly resembles the transference number plot for pure water in Fig. 1. On this basis, the lower end of the curve has been extended as shown by the dotted line. If this extrapolation is correct, the anion transference at zero wt. % UO_2Cl_2 closely approaches the value of the transference number of the anion at infinite dilution in pure water. However, the maximum for the anion transference number would be greater than one and would occur at twenty or greater weight per cent. The maximum transference number of greater than one in 99·7 per cent alcohol could be explained on the basis of the greater mobility of the $UO_2Cl_3^-$ ion as compared to the UO_2Cl^+ ion in the alcoholic solvent if the ions are assumed to have the same composition except for solvation in the two solvents. However, the ionic species might be different in the two solvents. The relative solvation of the two ions in the two different solvents could be such as to cause the equal mobility of the two ions in water solvent and a greater mobility of the anion in alcoholic solvent. The existence in water of the UO_2Cl^+ and $UO_2Cl_3^-$ ions have been proven using the spectrophotometric approach. These data will be presented in a later paper.

In Table 6 and Fig. 5 the moles of water transferred from anode to cathode have been extrapolated graphically to 10·24 wt. % UO_2Cl_2. The plot shows an initial

TABLE 6.—CALCULATED MOLES OF WATER TRANSFERRED FROM THE ANODE TO THE CATHODE COMPARTMENT AT 10·24 WEIGHT PER CENT UO_2Cl_2 IN SOLVENTS OF DIFFERENT COMPOSITION

Solvent comp. wt. % ethanol	N_W^F	p_s^m	N_W^F 10·24 %
0	0·20	0·7346	
0	−1·29	1·8055	
0	−1·13	1·8055	+0·60
0	−0·14	5·3000	
0	1·80	19·7192	
0	1·86	19·7205	
18·5648	4·55	10·2388	4·55
53·65124	0·703	15·3280	−0·30
54·2216	3·34	26·1308	
85·6611	1·24	12·2112	
87·5031	3·27	9·3502	+2·1

increase in moles transported with increasing ethanol up to about 19 weight per cent alcohol. The number of moles of water transported from anode to cathode then decreases to a minimum at about 53 weight per cent ethanol and then increases as the ethanol is increased up to 84 per cent ethanol, which is as far as the data extends. This change in water content of the anode as compared to the cathode could have arisen in one of two ways. Either alcohol could be transported in one direction or water in the other; or a net amount of alcohol could have been carried in one direction or a net amount of water in the other. The shape of the curve in Fig. 5

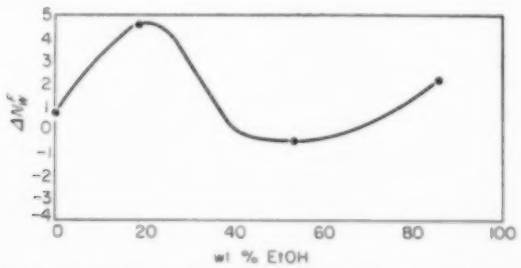

FIG. 5.—Calculated moles of water transfered from anode to cathode per F of electricity extrapolated to 10·24% UO_2Cl_2 plotted against per cent of EtOH in solution.

implies that the relative hydration of the cation as compared to the anion depends upon the weight per cent of ethanol in the solvent. This could result from differential dehydration or the differential alcoholation of the two ion species depending on the amount of alcohol in the solvent. More probably, it is a combination of the two. It would seem reasonable then that an outer layer of water of the larger volume anion ($UO_2Cl_3^-$) would be more susceptible to dehydration attack than would the outer layer of a lesser volume cation (UO_2Cl^+). It would also seem reasonable that the next most susceptible layer of water would be the outer layer of cation hydration. Reasoning further, the next most susceptible point of attack would be the inner

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TABLE 7.—PYCNOMETER AND DENSITY DATA AT 25·00 ± 0·01°C

All arm readings made with trademark facing observer pycnometer #1
43·16341 = weight empty corrected to a vacuum
0·000132 = 0·0001 reading on left arm
0·000141 = 0·0001 reading on right arm

Pycnometer #III
44·00861 = weight empty corrected to a vacuum
0·000112 = 0·0001 reading on left arm
0·000114 = 0·0001 reading on right arm

Wt. % EtOH	Density
14·32212	0·974392
18·48270	0·968585
29·03626	0·952449
54·08143	0·900776

solvation layer of water of the larger volume anion and the least susceptible to dehydration attack would be the inner hydration layer of the cation. Presumably, alcohol would tend to replace the removed water layers. These explanations could account for the sine curve as shown in Fig. 5.

In Table 7 are recorded some important data concerning the pycnometer and the densities of the water–ethanol system.

Precision and accuracy

The precision and accuracy of our measurements of densities and angles of rotation and the precision and accuracy of our analyses of the solutions were such that we feel our transference numbers are accurate to within one per cent or better. MACINNES[12] gives 0·4875 at 25°C for the transference number, measured by the Hittorf method, of the potassium ion in potassium chloride at a concentration of 1·0 equivalent per litre. The value of the transference number is only slightly dependent on concentration, being 0·488 at 0·50 equivalents per litre. Our value for the Hittorf transference number at 25°C for the potassium ion in potassium chloride at a concentration of 0·9891 equivalents per litre, is 0·488. See Table 3. This is a good indication of our precision and accuracy if the values quoted by MACINNES are accepted as valid. Our precision in measuring solvation numbers is indicated in Fig. 4 and Table 1. For example, compare the last item, $\Delta N_W{}^F$, in columns 2 and 3 and in columns 5 and 6 of Table 1.

[12] D. A. MACINNES, *The Principles of Electrochemistry* p. 85. Reinhold, New York (1939).

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 310 to 312. Pergamon Press Ltd. Printed in Northern Ireland

SOLUBILITIES OF Cs_2UCl_6, $Cs_2UO_2Cl_4$ AND Cs_2PuCl_6 IN HYDROCHLORIC ACID*

J. KOOI,† E. WEISSKOPF‡ and D. M. GRUEN
Argonne National Laboratory, Lemont, Illinois

(*Received* 20 *August* 1959)

Abstract—The solubilities of Cs_2UCl_6, $Cs_2UO_2Cl_4$ and Cs_2PuCl_6 have been determined in the concentration range 1–12 M HCl.

The possible use of Cs_2UCl_6 and Cs_2PuCl_6 as starting materials in the preparation of U and Pu metals is mentioned.

EXPERIMENTAL

Preparations. The double salt Cs_2UCl_6 was prepared by a method similar to that described by FERRARO.[1] Cesium chloride was added in 10 per cent excess over the stoichiometric amount to a U(IV) solution in 6 N HCl. Sufficient 6 N HCl was added to redissolve any precipitate. The solution was placed in a desiccator containing P_2O_5 and kept under about 1/3 of an atmosphere of N_2. After allowing evaporation and crystal growth to proceed for a week the supernatant was poured off, and the crystals washed with ethyl alcohol. The product was recrystallized once from 6 N HCl. The emerald green crystals after washing with ethyl alcohol, diethyl ether and carbon tetrachloride, were stored in a vacuum desiccator to prevent air oxidation.

$Cs_2UO_2Cl_4$ was prepared in exactly the same way as the tetravalent salt except that CsCl was added to a U(VI) solution in 6 N HCl. The slow evaporation step was carried out in air rather than in a N_2 atmosphere since there was no danger of oxidation in the case of the uranyl compound.

Cs_2PuCl_6 was prepared following the procedure of ANDERSON.[2] An approximately threefold excess of CsCl dissolved in 6 N HCl was added to a freshly prepared solution of Pu(IV) in 6 N HCl. Upon mixing the CsCl and Pu(IV) solutions, Cs_2PuCl_6 precipitated as a tan, finely divided, crystalline compound. After removing the supernatant, the precipitate was washed repeatedly with ethyl alcohol to remove water and excess cesium chloride. Finally, the Cs_2PuCl_6 was washed with diethyl ether and carbon tetrachloride, dried under a heat lamp and stored in a vacuum desiccator. Dicesium plutonium hexachloride prepared in this way is a free flowing, nonhygroscopic substance.

The Pu(IV) solution in one case (preparation 1) was prepared by repeatedly evaporating almost to dryness a solution of Pu(IV) and Pu(VI) nitrates in conc. HCl and finally making the solution 6 N in HCl. In another instance (preparation 2) about 1 g of Pu metal was dissolved in HCl, oxidized by means of hydrogen peroxide and then evaporated almost to dryness with HCl in a fashion similar to that described above.

Analyses. For Cs_2UCl_6 and $Cs_2UO_2Cl_4$ chemical analyses were carried out. Uranium was determined as U_3O_8; chlorine as AgCl. For Cs_2UCl_6, the uranium content was found to be 33·3 per cent; the chlorine content 29·7. The theoretical values are 33·2 and 29·6 per cent respectively. The Cl/U mole ratio was found to be 5·99.

For $Cs_2UO_2Cl_4$, the uranium content was found to be 35·1 per cent; the chlorine content 20·0 per cent. The theoretical values are 35·2 and 20·9 per cent respectively. The Cl/U mole ratio was found to be 3·97.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission and presented in part at the 115th Meeting of the Electrochemical Society, May 3–7, 1959, Philadelphia, Pennsylvania.

† On leave from Reactor Centrum Nederland.

‡ Student Aide, Summer 1958.

[1] J. FERRARO, *J. Inorg. Nucl. Chem.* **4**, 283 (1957).

[2] H. H. ANDERSON, *The Transuranium Elements* (Edited by G. T. SEABORG, T. J. KATZ and W. M. MANNING) NNES, Plutonium Project Record, Vol. 14B, Paper 6.13. McGraw Hill, New York (1949).

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With Cs_2PuCl_6 an X-ray powder pattern was obtained. This pattern contained only the well-known lines of the pure compound. No CsCl lines were observed.

Measurements. The solubilities of the three compounds were determined separately by analysing aliquots of solutions of known HCl concentrations equilibrated with the salts present in excess. In the case of Cs_2UCl_6 1 ml portions of HCl solutions were equilibrated with the compound in glass stoppered test-tubes, the air having been replaced by nitrogen. Analyses for uranium were carried out on 500 λ samples. The same procedure was used in the case of $Cs_2UO_2Cl_4$. With both substances, measurements were carried out at ambient room temperatures.

Solubility measurements on Cs_2PuCl_6 were carried out with the stoppered test tubes in a thermostated water bath at 25°C. Several independent sets of experiments were performed starting with a known amount of HCl of known strength in each case. The hydrochloric acid solution was equilibrated with Cs_2PuCl_6 and after sampling was diluted with a known amount of distilled water. Equilibration was allowed to proceed after which the solution was sampled again and diluted once more. The procedure was repeated until only a small amount of the salt phase remained in the tube. For each run the final HCl concentration was determined and was found to agree within the limits of experimental accuracy with the calculated value for each run. Plutonium analyses were performed by taking 10 λ aliquots which were α-counted after suitable dilution. The plutonium concentration was calculated using the value $7{\cdot}09 \times 10^4$ counts per min per γ for the specific activity of plutonium.

RESULTS AND DISCUSSION

The experimentally determined solubilities are given in Tables 1, 2 and 3.

TABLE 1.—SOLUBILITY OF Cs_2UCl_6 IN HCl

HCl Concentration (mole/l.)	Solubility (mole/l.)
1·00	1·515
2·00	1·257
4·00	0·756
5·00	0·548
6·00	0·339
6·05	0·328
8·00	0·129
9·00	0·060
10·00	0·029
11·00	0·016
11·50	0·016
12·10	0·012

TABLE 2.—SOLUBILITY OF $Cs_2UO_2Cl_4$ IN HCl

HCl Concentration (mole/l.)	Solubility (mole/l.)
1·00	1·216
2·00	0·962
3·50	0·550
5·00	0·278
7·00	0·100
10·00	0·046
11·50	0·032

TABLE 3.—SOLUBILITY OF Cs_2PuCl_6 IN HCl AT 25°C

HCl concentration (mole/l.) (Preparation 1)	Solubility (mole/l.) (Preparation 1)	HCl concentration (mole/l.) (Preparation 2)	Solubility (mole/l.) (Preparation 2)
12·08	0·0035	7·02	0·0257
10·88	0·0042	5·80	0·0622
9·94	0·0061	4·93	0·1321
9·10	0·0079	4·26	0·200
8·43	0·0091	3·73	0·267
7·78	0·0118	2·98	0·413
7·25	0·0185	1·97	0·603
6·75	0·0228	1·17	0·808
6·38	0·0271		
5·95	0·0330		
7·02	0·0197		
5·80	0·0530		

It can be seen that the solubility of Cs_2PuCl_6 is lower than the Cs_2UCl_6 or the $Cs_2UO_2Cl_4$ solubility over the entire hydrochloric acid concentration range. The solubility of the uranyl salt is less at low hydrochloric acid concentration and greater at high hydrochloric acid concentrations than the solubility of the uranium (IV) salt. The cross-over point occurs in the neighborhood of 9 M HCl. In 6 M HCl, the solubility of Cs_2PuCl_6 is less by factors of five and ten respectively compared to the $Cs_2UO_2Cl_4$ and Cs_2UCl_6 solubilities at the same hydrochloric acid concentration.

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Some thoughts concerning Cs_2UCl_6 *and* Cs_2PuCl_6 *as starting materials for uranium and plutonium metal preparation*

The use of fluorides rather than chlorides as starting materials for uranium and plutonium metal production is due in large measure to the greater ease of handling of the nonhygroscopic fluorides compared with the hygroscopic uranium and plutonium chlorides. Unlike the simple chlorides, however, the double chlorides Cs_2UCl_6 and Cs_2PuCl_6 are *nonhygroscopic*. This property together with the ease of preparation and the modest solubility of these anhydrous salts merit their being considered as starting materials for uranium and plutonium metal preparation.

Because of (α,n) reactions on fluorine and lithium, these two elements are objectionable constituents in a Pu metal process. Thus BLUMENTHAL[3] finds a fast neutron flux of 20 neutrons cm^{-2}/min^{-1} outside a glovebox at a distance of about 1 ft from an electrolysis cell containing LiCl–KCl eutectic and about 100 g of PuF_4. This flux represents the maximum permissible dosage for a 40 hr week.

A process for plutonium metal production involving electrolysis of a solution of Cs_2PuCl_6 in molten CsCl carried out at 700°C could yield liquid plutonium metal while completely circumventing the neutron hazard. Experiments along these lines are in progress.

Acknowledgement—We thank S. SIEGEL of the Chemistry Division for obtaining the X-ray diffraction patterns of Cs_2PuCl_6.

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REACTIONS OF IODINE IN LIQUID AMMONIA*

G. W. WATT and D. R. FOERSTER†
Department of Chemistry, The University of Texas, Austin 12, Texas

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Abstract—The products of the interaction of iodine and liquid ammonia at −75° are NH_4I and $NI_3 \cdot 12NH_3$; at −33·5° a (probably) less highly ammoniated NI_3 is the stable solid phase, while at 25° iodine oxidizes ammonia to elemental nitrogen. The reactions between NI_3 and liquid ammonia solutions of potassium amide and potassium at −33·5° have been shown to yield KI, N_2 and NH_3, and KI and N_2, respectively. These studies lead also to the conclusion that the products of the interaction of iodine and liquid ammonia over the range −75 to 25° do not include any simple ionic I^{n+} species.

THE nature of "solutions" of iodine in liquid ammonia and reactions of iodine in this medium have been the subject of numerous and conflicting views,[1–11] most of which are based upon incomplete or otherwise insufficient experimental evidence. The experiments described below were undertaken to resolve these uncertainties.

EXPERIMENTAL

All materials employed were either anhydrous reagent grade chemicals or were purified to the equivalent specifications prior to use. Reactions in liquid ammonia at room temperature were carried out in sealed Pyrex tubes; reactions at lower temperatures were studied using equipment and procedures described in earlier papers from this laboratory.[12] In either case, anhydrous oxygen-free conditions were maintained unless otherwise indicated.

The interaction of iodine and liquid ammonia at −75 *to* 25°

At −75°, ca. 5 ml of ammonia was condensed on 1·270 g of iodine, the tube was sealed and allowed to warm to 25°. As the temperature increased, the solid that was rust-coloured at −75° changed to a green solid that was consumed slowly as the reaction progressed. The initially colourless solution became successively yellow, orange, yellow and colourless, while 38·0 cc of nitrogen [calc. (equation 8): 37·4 cc] was evolved. Evaporation of the ammonia left 1·44 g of ammonium iodide [calc. tequation 8): 1·45 g] which was identified by analysis (Found: I, 87·5; Calc. for NH_4I: I, 87·6%) and by an X-ray diffraction pattern that included no extraneous lines.

The identity of the rust-coloured solid that formed at −75° was established as $NI_3 \cdot 12NH_3$ as follows. A 0·541 g sample of iodine was sealed in an 18 mm o.d. Pyrex tube provided with a fritted glass filter through which an excess of anhydrous liquid ammonia was condensed at −75°. When

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† Present address: Department of Chemistry, The University of Missouri, Columbia, Mo.

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conversion of the iodine appeared to be complete, the solid was filtered and washed three times with 10 ml portions of liquid ammonia. The pressure was reduced to ca. 10^{-3} mm for 1 hr to remove the solvent completely; thereafter the segment of the tube containing the solid was sealed off and transferred to a small Monel metal autoclave pre-cooled to −75°. (Throughout all of the preceding operations, the temperature of the solid sample was maintained at −75°.) The autoclave was sealed, evacuated and then heated slowly to 100°; the tube containing the sample exploded as the temperature was raised. Analytical data were obtained as follows. The nitrogen and ammonia liberated were removed with a Toepler pump and their volumes determined by absorbing the ammonia in water, measuring the corresponding volume decrease and then measuring the volume of the residual nitrogen. The solid residue from the autoclave was analysed for ammonium ion and for iodine (as iodide ion) following reduction with sodium hydrogen sulphite. (Found: I, 63·1; N, 30·8; H, 6·15. Calc. for $NI_3 \cdot 12NH_3$: I, 63·7; N, 30·4; H, 6·01%).

Reactions at −33·5°

Preliminary experiments. Condensation of ammonia on iodine at −33·5° resulted in the formation of a black liquid which was slowly converted to an olive-green crystalline solid and a pale yellow solution, without evolution of any water-insoluble gas. After 45 hr, the solvent was evaporated and a red-black oily liquid remained unchanged even after being subjected to reduced pressure (ca. 10^{-3} mm) for several hours. After brief exposure to the atmosphere, this product was dried over concentrated sulphuric acid, whereupon a violet-coloured solid formed. Analysis of a representative sample accounted for 65 per cent of the initial iodine as elemental iodine and 26 per cent as iodine ion. The absorption spectrum of a sample of this product in carbon tetrachloride was compared with the spectra of iodine in carbon tetrachloride and iodine plus ammonium iodide in the same solvent. These spectra were identical in the visible region, but the product from the reaction with ammonia showed a broad band in the near ultra-violet.

In a similar experiment, the olive-green solid referred to above was separated by filtration and washed with liquid ammonia. As the solid product was warmed from −33·5 to 25°, a gas was evolved, and the solid changed to a red-black substance. After standing out of contact with the atmosphere for 3 hr, this solid exploded violently and demolished all of the equipment in the immediate vicinity. Analysis of the black liquid residue remaining after evaporation of the solvent from the combined filtrate and washings showed that the distribution of the initial iodine between the ammonia-insoluble and ammonia-soluble products was 1 : 1.

For the purpose of determining whether the products of the iodine-ammonia reaction at −33·5° included any cationic iodine, cation exchange experiments were carried out in a manner similar to that described by KEENAN and MCDOWELL[13] for the use of cation exchange resins in liquid ammonia. Dowex 50W was dried thoroughly and then extracted exhaustively with anhydrous liquid ammonia prior to use. Approximately 3 g of this resin was added to 1·132 g of iodine in 40 ml of liquid ammonia at −33·5° and stirred for 20 hr in a closed system. The resin was separated and washed with liquid ammonia. Analysis of the combined filtrate and washings accounted for 1·125 g of iodine, or 99·4 per cent of that used. In independent experiments it was established that, as evidenced by maintenance of total capacity, the resin was unaltered during this treatment. Since it is known that pyridine forms stable complexes with cationic iodine,[14] dry pyridine was added to the products of the interaction of iodine and liquid ammonia at −33·5°. There was no evidence of reaction.

Potentiometric titrations. In order to explore the reactivity of the products of interaction of iodine and ammonia toward an acidic, a basic, and a strongly reducing medium, potentiometric titrations in ammonia[12] were carried out as follows.

Iodine (0·500 g) in 60 ml of liquid ammonia was titrated with a 0·377 M solution of ammonium iodide in liquid ammonia at −40°. A total of 31·8 ml was added dropwise without visual evidence of reaction or significant change in potential.

Similarly, 0·118 g of iodine was added to 70 ml of ammonia at −36° and titrated with 0·110 M potassium amide solution. As each increment of the titrant was added, a transient pink colour appeared at the point of contact of the two solutions. The pale yellow colour of the solution of the iodine–ammonia reaction products was dissipated rapidly, but the olive-green solid was consumed only slowly and persisted until a total of one molar equivalent of the titrant had been added. After

[13] C. W. KEENAN and W. J. MCDOWELL, *J. Amer. Chem. Soc.* **75**, 6348 (1953).
[14] J. KLEINBERG, E. COLTON, J. SATTIZAHN and C. A. VAN DER WERF, *J. Amer. Chem. Soc.* **75**, 442 (1953).

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addition of 4 ml of the amide solution, the reaction mixture became slightly turbid; this turbidity increased as the titration proceeded and finally a trace of light gray flocculent solid was evident.* The titration data are shown in Fig. 1; the only significant change in potential corresponds to an observed end-point at 9·1 ml, as compared with 8·5 ml calculated for one one equivalent of titrant.

The data for a typical titration of 0·277 g of iodine in 60 ml of ammonia at −39° with 0·219 M potassium solution are also shown in Fig. 1; the observed end-point at 9·7 ml is to be compared with 9·9 ml calculated for one equivalent of titrant. During the course of the titration, both the pale

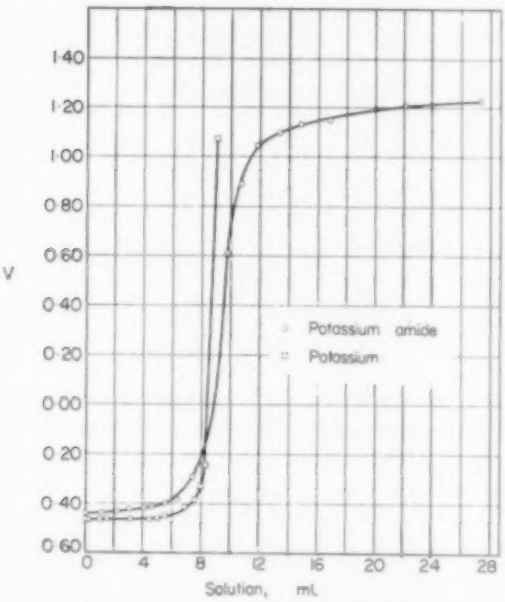

FIG. 1.—Potentiometric titration of iodine in liquid ammonia with liquid ammonia solutions of potassium and potassium amide.

yellow colour of the solution and the olive-green solid were replaced slowly by a slightly turbid solution as the titrant was consumed rapidly.

Large-scale reactions with potassium amide. In order to provide quantities of reaction products sufficient for separation and identification, 5·594 g of iodine in 30 ml of ammonia at −36° was treated dropwise with 2·46 g of potassium amide in 17·9 ml of ammonia. The observations were essentially the same as those described above; 164 cc of nitrogen and a negligible quantity of hydrogen were evolved. Evaporation of the solvent yielded 7·36 g of potassium iodide [calc. (equation 4): 7·32 g], the identity of which was established by an X-ray diffraction pattern and by analysis. (Found: K, 24·0; I, 72·3. Calc. for KI: K, 23·5; I, 76·5%). On the basis of the nitrogen evolved, the I/N ratio is essentially 3·00. Aqueous solutions of the reaction products were tested qualitatively for the presence of hydrazine using both the *p*-dimethylaminobenzaldehyde[13] and potassium hexachloroplatinate(IV) reagents; the results were negative in all cases.

In separate experiments, the interaction of potassium amide and the olive-green solid was examined as follows. After 7·466 g of iodine had reacted completely in 50 ml of ammonia at −35°, the mixture was filtered and the olive-green solid was washed with 15 ml of ammonia. The combined filtrate and washings was found to contain 3·89 g or 52·1 per cent of the iodine used. The olive-green solid was treated with 1·92 g of potassium amide in 20 ml of ammonia at −35°; again, the same observations

* The separation of this material was observed in all reactions with potassium amide and those with potassium also. The quantity that separated however was never sufficient for separation and characterization.

[13] G. W. WATT and J. D. CHRISP, *Analyt. Chem.* **24**, 2006 (1952).

were made and 212 cc of nitrogen and a trace of hydrogen were evolved. Iodine found by analysis amounted to 3·68 g; I/N, 1·53. Qualitative tests for hydrazine were negative.

Large-scale reactions with potassium. In a similar manner, 3·00 g of iodine in 40 ml of ammonia at −36° was treated with 1·00 g of potassium in 11 ml of ammonia; 40·8 cc of nitrogen and 111 cc of hydrogen were collected. Potassium iodide was identified by means of an X-ray diffraction pattern following evaporation of the solvent. From the above data, the following reaction ratios were computed: K/I, 1·09; I/N, 6·49; I/H, 2·38.

The action of potassium solution upon the olive-green solid was studied separately by preparing the latter from 4·504 g of iodine and 50 ml of ammonia at −36°, filtering, and washing the solid with 15 ml of ammonia. The combined filtrate and washings was found to contain 2·20 g or 48·9 per cent of the iodine used. The olive-green solid was treated with 15·0 ml of ammonia solution containing 0·738 g of potassium at −36°; 66·8 cc of nitrogen and 17·8 cc of hydrogen were liberated. After evaporation of the solvent from the colourless solution, the total iodine content of the residue was found to be 2·29 g; K/I, 1·08; I/N, 2·94.

DISCUSSION

The results reported above show that MOISSAN's conclusion[5] that iodine is unreactive toward liquid ammonia at −70°, and that reports by GORE[1] and FRIEDRICHS[6] that iodine "dissolves" completely in this solvent are incorrect. Furthermore, although the hypothesis that the I_2–NH_3 system involves the equilibrium,

$$I_2 + 2NH_3 \rightleftharpoons INH_2 + NH_4I \qquad (1)$$

may be attractive in connection with the interpretation of reactions between iodine and organic substances in liquid ammonia,[7,8,9] the present experiments provide no evidence whatever in support of this interpretation. Indeed, the experiments described above appear to rule out the existence of any simple I^{n+} species in liquid ammonia–iodine mixtures over the temperature range −75 to 25°.

The composition of the rust-coloured solid that is formed at −75° has been shown to correspond to the formula, $NI_3 \cdot 12NH_3$. Complete analysis of the products remaining after the confined explosive decomposition of a sample of the pure solid provided data that are wholly compatible with the formula given, but not with any ammoniate of iodoamine. Although these data do correspond reasonably well to the 8-ammoniate of diiodoamine, there are no other data or observations to indicate the presence of any such entity in the systems in question. The present data together with the work of HUGOT[4] show that the interaction of iodine and liquid ammonia at temperatures below −33·5° may be represented by,

$$3I_2 + xNH_3 \rightarrow NI_3 \cdot yNH_3 + 3NH_4I \cdot zNH_3 \qquad (2)$$

Both NI_3 and NH_4I form series of ammoniates.[4,16]

CADY[2] proposed that the reaction between iodine and liquid ammonia at −33·5° results in the formation of HN_3I and NH_4I in a mole ratio of 1 : 8. The present experiments however demonstrate that the distribution of iodine between ammonia-soluble and ammonia-insoluble species is 1 : 1 and are otherwise compatible with the equation (where ammoniation is neglected),

$$6I_2 + 8NH_3 \rightarrow 2NI_3 + 6NH_4I \qquad (3)$$

These products should be expected to be unreactive toward ammonia solutions of ammonium iodide, and such was found to be the case.

[16] G. W. WATT and W. R. MCBRIDE, *J. Amer. Chem. Soc.* **77**, 1317 (1955).

All of the available data relative to the reaction between iodine and potassium amide in ammonia at −33·5° are compatible with the over-all reaction,

$$3I_2 + 6KNH_2 \rightarrow 6KI + N_2 + 4NH_3 \quad (4)$$

which was suggested by BERGSTROM[7] on the basis of observations made under conditions such that potassium amide was always present in excess. In the present case, the potentiometric titration data (Fig. 1) imply that the rates of reaction of KNH_2 with NH_4I and NI_3 are roughly comparable and the results of the large-scale reactions show that the latter reacts as follows,

$$NI_3 + 3KNH_2 \rightarrow 3KI + N_2 + 2NH_3 \quad (5)$$

Failure to detect hydrazine as a product of these reactions essentially eliminates INH_2 as a product of the interaction of iodine and ammonia at −33·5°. Following completion of the present experiments, JANDER and SCHMID[11] described experiments on the interaction of NI_3 and KNH_2 in ammonia at −78°. At this temperature, they observed the transitory existence of a red solution attributed to KHNI which decomposed to yield nitrogen and potassium iodide. Still more recently, JANDER and SCHMID[17] have reported that $NI_3 \cdot 3NH_3$ and $NI_3 \cdot NH_3$ are the only stable ammoniates that they were able to isolate at −78 and 30°. They refer however to a "red substance" observed at −78°. This is probably the phase described above as a rust-brown solid and shown to be the 12-ammoniate. It is also evident from the work of JANDER and SCHMID that the explosive green-crystalline solid described above is the 3-ammoniate.

Potentiometric titration, analytical and X-ray diffraction data presented above are in accord with the conclusion that the over-all reaction between iodine in liquid ammonia at −33·5° and ammonia solutions of potassium may be represented by,

$$6I_2 + 12K^+ + 12e^- + 2NH_3 \rightarrow 12KI + 3H_2 + N_2 \quad (6)$$

One half of the potassium consumed in reaction (6), however, merely serves to reduce the NH_4I formed via reaction (3); the remainder reacts with NI_3 as follows,

$$NI_3 + 6K^+ + 6e^- \rightarrow 6KI + N_2 \quad (7)$$

Even though VAUGHN and NIEUWLAND[10] did not maintain anhydrous conditions or report adequate supporting data, the results given above show that their interpretation of the over-all reaction between iodine and liquid ammonia at 25° is correct, i.e.

$$3I_2 + 8NH_3 \rightarrow 6NH_4I + N_2 \quad (8)$$

[17] J. JANDER and E. SCHMID, *Angew. Chem.* **71**, 31 (1959).

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CHEMISTRY OF PHOSPHORUS ALUMINIUM BONDING: DIMETHYLPHOSPHINO–ALUMINIUM HYDRIDES AND CHLORIDES*

A. B. BURG and K. MÖDRITZER**
Department of Chemistry, University of Southern California
Los Angeles 7, California

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Abstract—The solvolysis of Al–H compounds in liquid dimethylphosphine leads to $(CH_3)_2P$–Al bonding. The composition $(CH_3)_2PAlH_2 \cdot (CH_3)_2PH$ was formed from $LiAlH_4$ with $(CH_3)_2PCl$ in liquid $(CH_3)_2PH$; and more extensive phosphinolysis occurred with $AlCl_3 + LiAlH_4$ (proportions to form AlH_3) in liquid $(CH_3)_2PH$. Ether solutions were not suitable, for the ether competed in complex formation: only moderately phosphinolysed AlH_3 polymers were obtained. The phosphinolysis of $LiAlH_4$ was extensive, with indication of $LiHAl[P(CH_3)_2]_3$ as a distinct substance. The compositions $HAlCl_2$ and H_2AlCl were formed in ether and heated in liquid $(CH_3)_2PH$ to form benzene-soluble products having compositions represented by the formulas $(CH_3)_2PAlCl_2$ and $[(CH_3)_2P]_2AlCl$ (mol. wts. uncertain). These seemed to disproportionate during attempts at sublimination *in vacuo*, with chloride enrichment in the sublimates.

THE chemistry of P–Al bonding has not been extensively studied. As a contribution to the lore of the subject, we have developed methods for making some new phosphino-aluminium hydrides and chlorides. Unfortunately their properties did not permit gas-phase molecular weight determinations, nor did the period of our collaboration afford enough time for trustworthy determinations of colligative properties; hence the interesting question of their molecular character can be answered only by further work which is not immediately feasible. However, the conditions required for their synthesis were not easily found, and accordingly seem worthy of description at this time.

It was initially supposed that a composition such as $(CH_3)_2PAlH_2$ might be made through formation of the complex $(CH_3)_2PH \cdot AlH_3$, which was expected to exist because dimethylphosphine acts as a strong base toward the BH_3 group[1] and even makes a fairly strong bond to the $Al(CH_3)_3$ unit.[2] Also favourable was the existence of fairly stable tertiary-amine complexes of AlH_3.[3,4] However, the first experiments indicated that AlH_3 etherates and the etherated AlH_3 polymer are stabler than any $(CH_3)_2PH$–AlH_3 complex, for no such complex could be formed from ether solutions of AlH_3 or from complexes having higher stability than the AlH_3 polymer. The permanently monomeric tetrahydrofuran complex $C_4H_8OAlH_3$ reacted with $(CH_3)_2PH$

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** Present address: Inorganic Chemicals Division, Research Department, Monsanto Chemical Co., St. Louis 66, Missouri.

[1] A. B. BURG and R. I. WAGNER, *J. Amer. Chem. Soc.* **75**, 3872 (1953).
[2] N. R. DAVIDSON and H. C. BROWN, *J. Amer. Chem. Soc.* **64**, 316 (1942).
[3] E. WIBERG, H. GRAF and R. USÓN, *Z. Anorg. Chem.* **272**, 221 (1953).
[4] E. WIBERG and H. NÖTH, *Z. Naturf.* **10** b, 237 (1955).

to produce a phosphino-polymer of average composition $(CH_3)_2PAl_5H_{14}$, not necessarily supporting the idea that a $(CH_3)_2PH$–AlH_3 complex occurred as a transition stage of the reaction. The instability of such a complex would correlate with the observation that $(C_2H_5)_3PAlH_3$ is unstable.[5] It would also lend further substance to the suggestion that BH_3 complexes of phosphorus bases owe much of their stability to interaction of the B-H bonding electrons with suitable 3*d* orbitals of phosphorus,[6] a situation not effectively imitated by Al–H bonding electrons.

Experiments depending upon the strongly hydridic Al–H bond to react with the very slightly available proton from the free dimethylphosphine[7] were only partially successful. Aside from the above-mentioned case of the tetrahydrofuran complex, there was a slow but eventually fairly extensive phosphinolysis of lithium aluminium hydride in solution in liquid dimethylphosphine; however, only a moderately phosphinolysed aluminium hydride polymer resulted from a reaction between $(CH_3)_2PH_2Cl$ and $LiAlH_4$, also in liquid dimethylphosphine.

Better results were obtained from a reaction between lithium aluminium hydride and aluminium chloride, in the 3 : 1 ratio required to make AlH_3,[8] directly in liquid dimethylphosphine as the solvent. Here there was nothing to interfere with P–Al complex-formation, which would promote the protic-acid action of the P–H bond. In this case the replacement of Al–H bonds by Al–P bonds went a little beyond the composition $(CH_3)_2PAlH_2$. A somewhat neater result was obtained from the reaction of $LiAlH_4$ with $(CH_3)_2PCl$,[9] to form $(CH_3)_2PAlH_2{\cdot}(CH_3)_2PH$.

It was considered that the chloroaluminium hydrides H_2AlCl and $HAlCl_2$[10] might be phosphinolysed more easily than AlH_3 because the stronger Al–P complex bonding would enhance the protic-acid activity of the P–H bond. Accordingly the etherates of these chloroaluminium hydrides were made and dissolved in liquid dimethylphosphine; then at slightly elevated temperatures the solutions formed hydrogen in amounts corresponding to the formation of $(CH_3)_2PAlCl_2$ and $[(CH_3)_2P]_2AlCl$. These products had only metastable solubility in dimethylphosphine but proved to be soluble in benzene. However, the initial attempts at molecular weight determination gave uncertain results because the presence or absence of residual solvent dimethylphosphine could not be demonstrated quite surely. Both products seemed to disproportionate on heating *in vacuo*, forming sublimates richer in chloride and residues richer in $(CH_3)_2P$ groups.

DIMETHYLPHOSPHINO-ALUMINIUM HYDRIDES

Phosphinolysis of aluminium hydride in ethers. A 1 mmole solution of AlH_3 in diethyl ether was made from $LiAlH_4$ and $AlCl_3$ (3 : 1 ratio)[8] and treated with 4·68 mmole of $(CH_3)_2PH$ in the high vacuum system. After two days at room temperature the volatile components were distilled off and all of the $(CH_3)_2PH$ was recovered as the slightly volatile hydrochloride.[11] The only reaction had been polymerization of the aluminium hydride; and the polymer was not phosphinolysed at all.

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[8] A. E. Finholt, A. C. Bond, Jr. and H. I. Schlesinger, *J. Amer. Chem. Soc.* **69**, 1199 (1947).
[9] A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.* **80**, 1108 (1958).
[10] E. Wiberg and M. Schmidt, *Z. Naturf.* **6** b, 460 (1951); E. Wiberg, *Angew. Chem.* **65**, 22 (1953).
[11] H. C. Brown, *J. Amer. Chem. Soc.* **67**, 503 (1945).

Next tetrahydrofuran (THF) was tried, as a solvent in which AlH_3 does not polymerize so easily. A solution of 1·20 mmole of AlH_3 in 2 ml of THF was heated with 4·82 mmole of $(CH_3)_2PH$ in a sealed tube for seven days at 60°, forming white crystals which did not increase after the first two days. The resulting H_2 was measured as 0·26 mmole and the recovery of 4·58 mmole of $(CH_3)_2PH$ meant that 0·24 mmole had been used. Thus the empirical formula of the non-volatile product was close to $(CH_3)_2PAl_5H_{14}$. The very limited extent of the phosphinolysis, and its failure to continue after two days, would indicate that AlH_3–polymer formation had largely supervened; however some phosphinolysis had occurred before the polymerization could be completed.

Results with liquid dimethylphosphine as solvent. Aluminium hydride was formed and phosphinolysed directly in $(CH_3)_2PH$ as the solvent, in order to minimize interference with the formation of the presumed intermediate, the complex $(CH_3)_2PH{\cdot}AlH_3$. $LiAlH_4$ was dissolved in ether, filtered and vacuum-evaporated with baking at 100° to remove all ether; then this fresh $LiAlH_4$ (2·57 mmole) was treated in a sealed tube with 2·57 mmole of $(CH_3)_2PH_2Cl$ and 38·48 mmole of $(CH_3)_2PH$. Hydrogen and a gelatinous precipitate were formed. After six days at room temperature the H_2 was measured as 3·11 mmole, of which 2·57 would have represented the formation of AlH_3 from $LiAlH_4$; hence the phosphinolysis reaction could have used only 0·54 mmole of the available 41·05 mmole of $(CH_3)_2PH$. But the actual recovery of only 39·91 mmole of $(CH_3)_2PH$ left 1·14 mmole to be accounted for. Hence the empirical formula of the product was roughly $(CH_3)_2PAlH_2$–$4AlH_3$–$1{\cdot}11(CH_3)_2PH$, representing the same extent of phosphinolysis as when THF was the solvent.

In a second experiment based upon the same plan, 1·08 mmole of AlH_3 (from 0·81 mmole of $LiAlH_4$ and 0·27 mmole of $AlCl_3$), in 25·35 mmole of $(CH_3)_2PH$, gave 1·29 mmole of H_2 during a two-day heating at 50°; thus phosphinolysis went beyond the first stage. Nearly all the recoverable $(CH_3)_2PH$ came off *in vacuo* at room temperature and a trace more at 100°; then the empirical formula of the product was $(CH_3)_2PAlH_2$–$0{\cdot}25[(CH_3)_2P]_2AlH$–$1{\cdot}36(CH_3)_2PH$. An attempt to resolve this mixture, by a vacuum sublimation ending with flame-heating of the residue, led to some phosphine recovery, some H_2 formation, an aluminium mirror, and a white solid not easy to sublime. The attempt at analysis by basic hydrolysis disclosed neither Al–H nor Al–Cl bonds; but a real breakdown was not feasible. It probably was mostly $[(CH_3)_2P]_3Al$, which might well form an unreactive low polymer.

Dimethylchlorophosphine and lithium aluminium hydride. For a neater arrival at the $(CH_3)_2PAlH_2$ stage of phosphinolysis, the reaction $(CH_3)_2PCl + LiAlH_4 \rightarrow LiCl + (CH_3)_2PAlH_2 + H_2$ is suitable. A 1·05 mmole sample of $(CH_3)_2PCl$ was made by the aminophosphine method[9] and placed with 1·03 mmole of $LiAlH_4$ in 27·87 mmole of $(CH_3)_2PH$. After two days at 60° the mixture had formed 1·09 mmole of H_2; then the $(CH_3)_2PH$ was distilled off and determined as 26·74 mmole. Hence 1·13 mmole of $(CH_3)_2PH$ remained in the non-volatile white solid residue, the composition of which could be written as $(CH_3)_2PAlH_2$–$(CH_3)_2PH + LiCl$. The salt formulation $Li(CH_3)_2PAlH_2Cl$–$(CH_3)_2PH$ does not seem appropriate since the electron-acceptor tendency of the aluminium is far more likely to be satisfied by phosphorus than by chloride; and lattice-energy differences would favour the separation of LiCl. However, the presumed $(CH_3)_2PAlH_2$–$(CH_3)_2PH$ was not separated from the initially-precipitated LiCl, nor was it shown to be soluble in liquid $(CH_3)_2PH$. The solid product

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was observed to be stable on heating to 100°, but very reactive to air and moisture, giving the typical alkylphosphine odour.

Phosphinolysis of lithium aluminium hydride. Three experiments on the behaviour of $LiAlH_4$ in liquid $(CH_3)_2PH$ were terminated at different stages and the degree of phosphinolysis was estimated for each. In each case the $LiAlH_4$ was "freshened" by recovery from a clear ether solution, with removal of all ether by evacuation at temperatures as high as 100°. In the first experiment the phosphinolysis went as far as 35 per cent of one stage during 2 hr at room temperature. The second experiment ran two weeks at 80°, leading to the empirical formula $LiAlH_{2\cdot46}[(CH_3)_2P]_{1\cdot54}$. This product was heated *in vacuo* for 5 hr at 190°, yielding only a slight sublimate. The third experiment went for a week at 80°, producing $1\cdot688H_2$ per $LiAlH_4$; and the product retained $0\cdot429(CH_3)_2PH$ beyond that needed to form the hydrogen. The re-sealed tube was heated to 150° (two days), carrying the phosphinolysis a little farther but causing some decomposition; and the residue at 250° gave small sublimates difficult to interpret. The final residue had a $(CH_3)_2P$: Al : H ratio of 60 : 100 : 43, aside from some supposed LiH and carbon.

In a fourth experiment of this kind, 4·925 mmole of $LiAlH_4$, kept in 38·80 mmole of liquid $(CH_3)_2PH$ for a week at 50°, gave 1·01 mmole of H_2. The solid product, of empirical formula $LiAlH_{3\cdot795}[(CH_3)_2P]_{0\cdot205}$–$2\cdot90(CH_3)_2PH$, was heated at 90° in the resealed tube, which was placed nearly horizontal to permit the flow of molten material away from the solid. After three weeks the reopened tube delivered 13·55 mmole of H_2 (total now 14·56, representing 74 per cent of the Al–H bonds) and 3·01 mmole of $(CH_3)_2PH$. The drained-off molten material now was represented by a white solid which hydrolysed vigorously in water. Completion of this hydrolysis in a basic solution, with measurement of H_2 and $(CH_3)_2PH$, and analysis for aluminium by the 8-hydroxyquinoline method, led to the empirical formula $LiAlH_{0\cdot95}[P(CH_3)_2]_{2\cdot93}$. The possibility of obtaining $Al[P(CH_3)_2]_3$ from such a product remains interesting.

DIMETHYLPHOSPHINO-ALUMINIUM CHLORIDES

It was considered that $HAlCl_2$ and H_2AlCl would phosphinolyse more easily than AlH_3 because P–Al complex bonding would be more effective. In accord with this expectation it was found possible to form the new compositions $(CH_3)_2PAlCl_2$ and $[(CH_3)_2P]_2AlCl$ from the respective chloroaluminium hydrides. For such experiments the $HAlCl_2$ was made from AlH_3 with $2AlCl_3$ and the composition H_2AlCl was established by combining $2AlH_3$ with one $AlCl_3$— in both cases in ether solution.[12] Then the ether was removed as thoroughly as possible and the phosphinolysis of the resulting mono-etherate accomplished in liquid $(CH_3)_2PH$.

Dimethylphosphino-aluminium dichloride. In a preliminary trial, one $HAlCl_2$ with $11(CH_3)_2PH$, at 50° for three weeks, gave $0\cdot94H_2$, with recovery of $10\cdot0(CH_3)_2PH$. The resulting $(CH_3)_2PAlCl_2$, *in vacuo* at 150°, gave a sublimate analysed as $[(CH_3)_2P]_{0\cdot36}AlCl_{2\cdot69}$ and a residue having the empirical formula $[(CH_3)_2P]_{1\cdot42}AlCl_{1\cdot38}$. Evidently the most chlorinated disproportionation product was the most volatile.

In the next experiment, 1.35 mmole of $(CH_3)_2PAlCl_2$, made in the same manner, was heated *in vacuo* during 8 hr up to 420°, forming a sublimate analysing as $[(CH_3)_2P]_{0\cdot16}AlCl_{2\cdot84}$—almost pure Al_2Cl_6. The dark residue was base-hydrolysed for an analysis showing the defective composition $[(CH_3)_2P]_{1\cdot02}AlCl_{1\cdot29}$. Since there

[12] E. Wiberg and M. Schmidt, *Z. Naturf.* **6** b, 460 (1951).

was no formation of H_2 to indicate any kind of Al–Al bonding, it is possible that some of the product was inert toward the hot basic solutions.

Next an experiment was done with a three-way sealed tube permitting decantation, for crystallization and washing of the initial phosphinolysis product. The 2·272 mmole of $HAlCl_2$ etherate, after reaction in 20·31 mmole of $(CH_3)_2PH$ during a week at 60°, gave a small insoluble by-product—later analysed as $[(CH_3)_2P]_{1\cdot21}AlCl_{1\cdot78}$—from which the main product could be decanted off in solution. The solvent was evaporated into the third arm, leaving an oily colourless liquid which crystallized upon shaking and cooling. When the solvent was poured back, the crystals redissolved; but with repetition of the evaporation and return of solvent, the solute became less and less soluble, and finally quite insoluble. The analysis by basic hydrolysis gave the empirical formula as $[(CH_3)_2P]_{0\cdot94}AlCl_{2\cdot01}$, with no difficulty in the completion of the breakdown.

The change toward insolubility was first considered to be a conversion from a monomeric or low-polymeric $(CH_3)_2PAlCl_2$ to a higher polymer form, possibly through removal of ether from its bonding to aluminium. However, a new sample, treated in the same way, proved to be soluble in benzene, in which its apparent molecular weight was near to that of the monomer form. Five determinations, by the tensiometric method at a mole-fraction near 0·04, gave the mol. wt. as 161 ± 17 (calc. 159). Thus it would seem that the dissociation of an ether complex would explain the conversion to material insoluble in dimethylphosphine—and also in ether. However, it is not certain that the benzene-soluble monomer was not itself an ether complex, for the size of the sample was determined by the aluminium content.

Bis(dimethylphosphino)aluminium chloride. A preliminary trial of the $(CH_3)_2PH$–H_2AlCl reaction having shown that the process was incomplete after four days in liquid $(CH_3)_2PH$ at 50°, a better result was obtained from a two-week run at 60°: the 2·255 mmole sample of H_2AlCl etherate yielded 4·53 mmole of H_2 (calc. 4·51). The $[(CH_3)_2P]_2AlCl$ was observed first as a white precipitate clinging to the walls of the tube; then as the solvent was removed, transparent crystals were formed and later became opaque. The material was unchanged by heating at 150°, and at 200° (3 days) it only hardened and turned slightly yellow. In the open air at a low humidity it hydrolysed slowly; but with liquid water it reacted vigorously, with ignition of the resulting $(CH_3)_2PH$.

The phosphinolysis of H_2AlCl was done also in a sealed three-way decanting tube, using 1·644 mmole of H_2AlCl in 30·32 mmole of $(CH_3)_2PH$ (two days at 50°). Again the resulting solute became insoluble on standing. The initial precipitate was analysed as $[(CH_3)_2P]_{1\cdot98}AlCl$, whereas the solute showed a less advanced phosphinolysis. In another experiment, longer standing at 60° gave a solute analysed as $[(CH_3)_2P]_{1\cdot96}AlCl_{0\cdot98}$. As in the case of $(CH_3)_2PAlCl_2$, this bis(dimethylphosphino) aluminium chloride, after precipitation from liquid $(CH_3)_2PH$, dissolved in benzene. However, the mol. wt. determinations in benzene showed wide variations, with an uncertain trend suggestive of polymerization.

One sample approaching the composition $[(CH_3)_2P]_2AlCl$ was heated *in vacuo* at 170–180°, giving a sublimate not far from the composition $(CH_3)_2PAlCl_2$. Disproportionation seems to be a normal result of such attempts at purification.

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NOTES

The effect of dissolved air on the reduction of tracer level plutonium-IV by uranium-IV

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RYDBERG[1] has shown that 0·05 M solutions of uranous salts in 0·7 M HNO_3 will remove 95 ± 3% of tracer level plutonium from a solution of hexavalent and tetravalent plutonium in hexone, on shaking for 5 min in the absence of dissolved oxygen. In the presence of air, only 70 ± 10% of the plutonium is removed. This note shows that dissolved oxygen in the presence of excess uranium-IV causes a partial re-oxidation of plutonium-III to plutonium-IV, and offers an explanation.

Experimental

Materials

10^{-3} M Pu(IV) in 10 M HNO_3 was prepared from a concentrated stock and was shown by TTA assay to be at least 98·5% tetravalent.

Uranous nitrate was prepared by electrolysis at a mercury cathode, in the presence of sulphamic acid to suppress nitrite. Provided that nitrite is suppressed and that nitric acid is not less than 1 M, uranous nitrate solutions are much more stable than reported by RYDBERG,[1] e.g. 2×10^{-2} M U(IV) in 3 M HNO_3, 0·1 M sulphamic acid without removal of dissolved air lost only 14% of the U(IV) during 5 days storage in a clear glass flask in diffuse daylight.

Analysis

Residual Pu(IV) in reaction mixtures (3 M HNO_3) was extracted into an equal volume of 20% tributyl phosphate in odourless kerosene, centrifuged, and an aliquot was mounted for alpha counting. The results were corrected for the small extraction of Pu(III).[2]

Pu(IV) in solutions of lower acidity was separated by TTA extraction.[3]

Results

Rate of reduction of Pu(IV) *in the presence of air*

The results in Tables 1 and 2 were obtained in 3 M HNO_3, 0·1 M sulphamic acid at room temperature.

TABLE 1

Initial concentrations (M)		Time for 50% reduction (min)
Pu(IV)	U(IV)	
10^{-7}	10^{-5}	25–30
10^{-7}	10^{-4}	3–5
10^{-6}	10^{-4}	Less than 1

[1] J. RYDBERG, *J. Inorg. Nucl. Chem.* **5**, 79 (1957).
[2] G. F. BEST, H. A. C. MCKAY and P. R. WOODGATE, *J. Inorg. Nucl. Chem.* **4**, 315 (1957).
[3] J. G. CUNINGHAME and G. L. MILES, *J. Inorg. Nucl. Chem.* **3**, 54 (1956).

The half-lives reported in Table 1 are an order of magnitude less than those calculated for a perchloric acid solution, probably due to catalysis of the reaction by sulphamic acid or sulphuric acid.[4]

Residual levels of Pu(IV) *in the presence and absence of air*

The results in Table 2 were obtained after 2 hr reaction. Similar residual levels persisted on standing overnight. The higher amounts of U(IV) gave green solutions which were obviously stable over the period of the reaction. Some results with ferrous sulphamate are included for comparison.

TABLE 2

Initial concentrations (M)			Residual Pu(IV)(%)	
Pu(IV)	U(IV)	Fe(II)	In air	Under N_2
10^{-7}	10^{-5}	—	15	—
10^{-7}	10^{-4}	—	7·5	—
10^{-7}	10^{-3}	—	7	1
10^{-6}	10^{-4}	—	1·5	—
10^{-6}	10^{-3}	—	3	1
10^{-7}	—	2×10^{-3}	3	—
10^{-7}	—	2×10^{-2}	1·5	—
10^{-6}	—	2×10^{-3}	1·2	—
10^{-6}	—	2×10^{-2}	0·8	—

In the presence of dissolved air, the reduction with ferrous sulphamate is more complete than with an equivalent concentration of U(IV), but the latter reagent is practically quantitative in the absence of air.

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Re-oxidation of Pu(III) *by air in the presence of* U(IV)

An air-free solution of 10^{-2} M U(IV), 10^{-6} M Pu in 3 M HNO_3, 0·02 M sulphamic acid was stored under nitrogen for three days. Excess U(IV) was still present (green colour) and analysis under nitrogen showed only 0·5% Pu(IV). On bubbling air through the solution for 10 min it remained green but showed 4% re-oxidation to Pu(IV).

In a further experiment, 10^{-5} M Pu(IV) was reduced under nitrogen (99% complete) and then aliquots were diluted with various concentrations of nitric acid, containing dissolved air. The dilutions were 10^{-6} M Pu, 10^{-2} M U(IV), 2×10^{-2} M sulphamic acid. The extent of re-oxidation to Pu(IV) after 14 hr is shown (Table 3) to increase at lower acidities.

TABLE 3

HNO_3 (M)	0·3	0·9	2·1	3·0
Re-oxidation (%)	36	14	10	5

Application of counter-current solvent extraction to the reduction of Pu(IV) *and* (VI) *by* U(IV)

The residual Pu(IV) which escapes reduction by U(IV) in the presence of air may be extracted into 20% tributylphosphate and subsequently removed by stripping with a fresh portion of U(IV). In a laboratory mixer-settler with five extraction stages and five stripping stages (strip solution = 10^{-2} M U(IV) in 3 M HNO_3), >99·5% reduction was achieved of 10^{-6} M Pu(IV) or Pu(VI) in 0·25 M uranyl nitrate, 2 M HNO_3. The plutonium (mixed with some U(IV) was recovered quantitatively in the aqueous raffinate, and the solvent product contained uranium, free from plutonium. No precautions were taken to exclude air.

[4] T. W. NEWTON, *J. Phys. Chem.* **62**, 943 (1958); **63**, 1493 (1959).

Discussion

The re-oxidation of Pu(III) in 3 M HNO_3, 0·1 M sulphamic acid at room temperature requires dissolved oxygen *and* U(IV), and under certain conditions the yield of Pu(IV) actually *increases* when more U(IV) is added (Table 2, results for 10^{-6} M plutonium). It then appears that U(IV) has a dual role. It rapidly reduces Pu(IV) to Pu(III) in 3 M HNO_3 (and also Pu(VI) to Pu(III)—see the section on counter-current experiments) but it also acts as a catalyst in promoting the re-oxidation of Pu(III) by dissolved oxygen, the latter reaction occurring more readily at lower acidity. The active agent in the re-oxidation must be an intermediate product in the slow reaction between U(IV) and oxygen, studied by HALPERN and SMITH.[5] They have shown that this proceeds by a chain mechanism, involving UO_2^+ and HO_2 as chain carriers. UO_2^+ would not oxidise Pu(III), according to the known redox potentials, but the peroxide radical HO_2 is a likely agent. The rate of the reaction between U(IV) and O_2 is inversely proportional to the acidity: the higher stationary state concentration of HO_2 at lower acidities would explain the results in Table 3.

E. N. JENKINS

A.E.R.E., Harwell
Didcot, Berks

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[5] J. HALPERN and J. G. SMITH, *Canad. J. Chem.* **34**, 1419 (1956).

Compounds in the system TiO_2–Cr_2O_3–Fe_2O_3

(*Received* 28 *October* 1959)

RECENTLY a number of investigations into the system TiO_2–Cr_2O_3 have been reported. ANDERSSON, *et al.*[1] found the compounds $Ti_{n-2}Cr_2O_{2n-1}$ with n = 6, 7, 8 and 9, which are isomorphous with members of the homologous series Ti_nO_{2n-1} and V_nO_{2n-1}, and also a compound $Ti_2Cr_2O_7$ which has a different structure. The latter is in agreement with earlier investigations by HAMELIN.[2] A compound $TiCr_2O_5$ which could be expected to be isomorphous with $TiFe_2O_5$ and $TiAl_2O_5$ (pseudobrookite structure) was not found. ÅSBRINK *et al.*[3] found small crystals with the composition $TiCr_2O_5$, after melting TiO_2 and Cr_2O_3 together in an electric furnace. The structure, however, was of the V_3O_5 type, which is essentially different from the pseudobrookite structure. HAMELIN[4] reported the presence of an unknown compound W in the system TiO_2–Al_2O_3–Cr_2O_3; the composition of W is in the neighbourhood of $TiCr_2O_5$. HAMELIN's samples, however, do not seem to have reached a state of equilibrium and therefore the composition of this compound is not exactly known.

This paper describes some investigations into the system TiO_2–Cr_2O_3–Fe_2O_3. It is to be expected that samples of this system attain their equilibrium-states more easily than samples of the TiO_2–Al_2O_3–Cr_2O_3 system.

The results are given in Fig. 1.

All the samples studied reached their equilibrium states by firing at 1300°C in O_2. In the two-phase system TiO_2—Cr_2O_3, the Andersson structures $Ti_4Cr_2O_{11}$, $Ti_5Cr_2O_{13}$, $Ti_6Cr_2O_{15}$, $Ti_7Cr_2O_{17}$ and a homogeneous area were found. On the other hand prolonged heating of $Ti_4Cr_2O_{11}$ and $Ti_5Cr_2O_{13}$ resulted in disproportionation into the stable compounds $Ti_6Cr_2O_{15}$ and $Ti_2Cr_2O_7$. $TiCr_2O_5$ was not found. From a study of the X-ray diagrams after a few per cent of Fe_2O_3 were added to the Andersson structures, it followed that $Ti_4Cr_2O_{11}$ and $Ti_5Cr_2O_{13}$ had completely disappeared whereas the other phases were now clearly distinguishable. In $Ti_2Cr_2O_7$ about $\frac{2}{3}$ of the Cr^{3+} ions can be replaced by Fe^{3+} ions, without the structure undergoing any change. In the part of the diagrams with 33⅓ mol % TiO_2, Fe_2TiO_5 forms a region of solid solutions. In this compound 15 mol % Fe_2O_3 may be replaced by Cr_2O_3. Another solid solution area at 33⅓ mol % TiO_2 is found from 10 mol % $FeO_{1\cdot5}$ to about 45 mol % $FeO_{1\cdot3}$. This phase has the V_3O_5 structure and is

[1] S. ANDERSSON, A. SUNDHOLM and A. MAGNÉLI, *Acta Chem. Scand.* **13**, 989 (1959).
[2] M. HAMELIN, *Bull. Soc. Chim. Fr.* 1421 (1957).
[3] S. ÅSBRINK, S. FRIBERG, A. MAGNÉLI and G. ANDERSSON, *Acta Chem. Scand.* **13**, 603 (1959).
[4] M. HAMELIN, *Bull. Soc. Chim. Fr.* 1431 (1957).

therefore analogous to the compound W found by HAMELIN[4] and with the crystals $TiCr_2O_5$ found by ÅSBRINK *et al.*[2] Apparently $TiCr_2O_5$ is stabilized by Fe^{2+} ions, but its structure is not of the pseudobrookite type. A third possible structure having the formula $(A,B)_3O_5$ is mentioned by ÅSBRINK and MAGNÉLI,[5] namely Ti_3O_5. We attempted to obtain such a structure by firing the samples with 33⅓ mol % TiO_2 at 1300°C and quenching and also by tempering these samples at lower temperatures and quenching afterwards. These attempts were not successful.

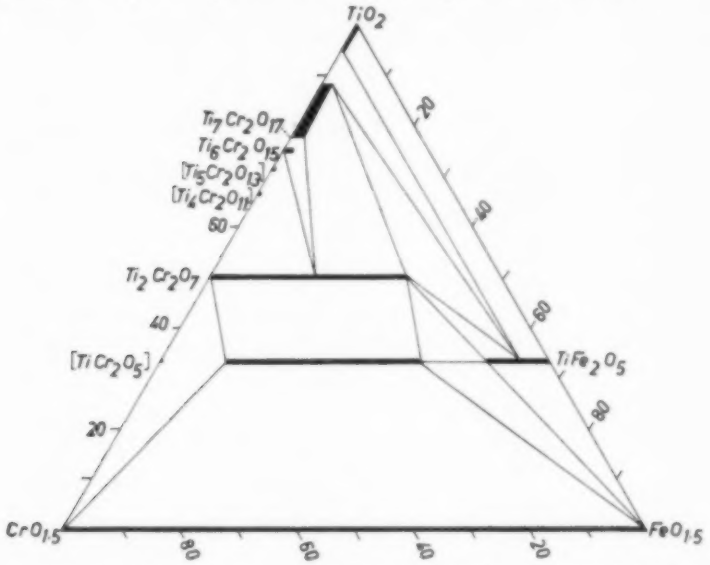

FIG. 1.—Diagram of the system TiO_2—Cr_2O_3—Fe_2O_3 at 1300°C. Formulae in brackets refer to compounds which are not stable at 1300°C.

Experimental

Mixtures of high purity specimens of TiO_2, Cr_2O_3 and Fe_2O_3 were wet-milled for 1 hr and heated to 1000°C for 15 hr. After cooling the pre-heated materials were milled again, pressed into disks and fired for 3 hr, generally at 1300°C in an O_2 atmosphere. The disks were quenched to room temperature and investigated with an X-ray diffractometer in order to identify the phases.

The samples in the region TiO_2–$Ti_2Cr_2O_7$ were investigated more thoroughly in both O_2 and N_2 atmospheres. They show little differences in the following properties: (i) their colours vary between dark yellow and brown (ii) they always contain a little amount of active oxygen (0·00–0·06 wt.%), (iii) their specific resistivity is high (10^5–10^8 Ω cm).

Philips Research Laboratories W. KWESTROO
N. V. Philips' Gloeilampenfabrieken A. ROOS
Eindhoven, Netherlands

[5] S. ÅSBRINK and A. MAGNÉLI, *Acta Cryst.* **12**, 575 (1959).

The preparation of diborane by the calcium hydride–boron halide reaction

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DIBORANE is readily prepared from reactions of lithium hydride or sodium hydride with excess boron trifluoride.[1,2]

[1] H. I. SCHLESINGER and H. C. BROWN *et al.*, *J. Amer. Chem. Soc.* **75**, 199, 209 (1953).
[2] H. C. BROWN and P. A. TIERNEY, *J. Amer. Chem. Soc.* **80**, 1552 (1958).

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It was the purpose of the present investigation to prepare diborane by a reaction between calcium hydride and a boron halide such as boron trifluoride or boron trichloride. By analogy from the postulated reaction steps for the production of diborane from lithium hydride or sodium hydride,[3] the following reactions would be necessary to generate diborane in a calcium hydride–boron halide system:

$$3Ca(BH_4)_2 + 2BX_3 \rightarrow 4B_2H_6 + 3CaX_2, \quad (1)$$

or

$$3Ca(BH_4)_2 + 8BX_3 \rightarrow 4B_2H_6 + 3Ca(BX_4)_2, \quad (2)$$

and

$$4B_2H_6 + 4CaH_2 \rightarrow 4Ca(BH_4)_2. \quad (3)$$

On the basis of these reactions it was sought to establish experimentally the steps in which

1. The $Ca(BH_4)_2$-BX_3 reaction forms B_2H_6,
2. B_2H_6 reacts with CaH_2 to produce more $Ca(BH_4)_2$, and
3. A $Ca(BH_4)_2$-seeded CaH_2-BX_3 system produces diborane in a one-step process.

Preparation and reactions of calcium borohydride

Calcium borohydride was prepared by the methods of KOLLONITSCH[2] and WIBERG.[4] The preparation of the borohydride by KOLLONITSCH's method using ethanol as a solvent at −40°C resulted in a low yield. A better yield (64%) was obtained by refluxing calcium chloride and sodium borohydride as a slurry in tetrahydrofuran (THF) at 65°C.

React ons of calcium borohydride with boron trichloride resulted in substantial yields of diborane in E-121 or THF as solvents. These reactions therefore satisfied the separate requirements of Steps 1 and 2.

TABLE 1.—SOLUBILITY OF $Ca(BH_4)_2$ IN ETHER SOLVENTS

Solvent	Solubility*
Monoglyme, E-121[a]	0·13
Diglyme, E-141[a]	2·05
Triglyme, E-161[a]	0·2
Dioxane	0·1
E-141, Et_2O 1 : 1 ratio by volume	0·38

* Grams $Ca(BH_4)_2$ per 100 g solvent.
[a] Ansul Chemical Company ethers: E-121-ethylene glycol dimethyl ether; E-141-diethylene glycol dimethyl ether, E-161-triethylene glycol dimethyl ether.

Solubility of calcium borohydride

The solubilities of calcium borohydride in several ether solvents were determined because various workers have speculated as to whether solubility is important for promoting reactions in these slurry systems. Table 1 lists the solubilities of calcium borohydride in g/100 g of solvent. It is interesting to note in answer to speculations on the importance of solubility that calcium borohydride is rather insoluble in monoglyme (E-121). Nevertheless, the reaction of calcium borohydride with boron trichloride in E-121 evolves diborane smoothly, and in moderately good yield (67 and 78 per cent)

In general, borohydrides have low solubility in most solvents; as the borohydride becomes more covalent and less salt-like, solubility decreases. It is evident that total solubility of calcium borohydride in these solvent systems is not directly related to the ability to generate diborane.

[3] J. KOLLONITSCH, O. FUCHS and V. GABOR, *Nature, Lond.* **173**, 125 (1954).
[4] E. WIBERG and R. HARTWIMMER, *Z. Naturf.* **10b**, 295 (1955).

Calcium hydride–boron trichloride reactions

Four reactions between boron trichloride and calcium hydride were carried out in E-121 and in THF at room temperature. Two reactions were for 20 hr and two were for 92 and 96 hr. In all cases only traces of diborane were produced. Analysis of the liquid products indicated that cleavage of the solvents was severe.[5] The rapid side reaction between boron trichloride and ethers therefore precludes the practicability of this reaction.

Calcium hydride–boron trifluoride reactions

A number of reactions were attempted with calcium hydride and boron trifluoride in THF, E-121, E-141, and E-161. Although these experiments yielded at least trace amounts of diborane, only two might be considered as successful experiments. In these two experiments the solvent was E-141; the conditions and net yield were as follows:

42 hr at 60–100°C	43% diborane
75 hr at 94–100°C	46% diborane

All these reactions required a calcium borohydride seed, but the reported net yield does not include diborane that would have been formed from the seed.

Solvents other than the four mentioned above were also investigated, but in no instance was diborane formed.

Conclusions

Diborane can be prepared from the reaction of calcium hydride and boron trifluoride. However, the yield and conditions for promoting the reaction are poor in comparison to preparations involving lithium hydride or sodium hydride. The results indicate the vast difference in reactivity between calcium hydride and sodium or lithium hydride.

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A. LEVY
J. B. VETRANO*
D. E. TRENT
J. F. FOSTER

Battelle Memorial Institute
Columbus 1, Ohio

* Present address: Atomics International, Canoga Park, California.

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Tetramethylammonium tetrafluoroborate

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ALTHOUGH it has been shown[1] that substituted ammonium tetrafluoroborates, R_4NBF_4 (R = Et, Pr^n, Bu^n), result from the reaction between tetra-alkylammonium halides and hydroxytrifluoroboric or methoxytrifluoroboric acids, it appears from the literature[2] that the corresponding reactions with tetramethylammonium halides yield tetramethylammonium hydroxytrifluoroborate. We have repeated these latter preparations and believe that the reaction of tetramethylammonium halides with hydroxy- or methoxy-trifluoroboric acids yields tetramethylammonium tetrafluoroborate. The salts were formerly characterised by analysis but the expected analytical figures for the two possible products are so similar (except for fluorine which is very difficult to determine accurately) that we do not consider that they constitute adequate proof of identity. The reported melting points of tetramethylammonium tetrafluoroborate, 418°,[1] and of tetramethylammonium hydroxytrifluoroborate, 414°,[2] are almost identical and again do not give a great deal of information.

[1] C. M. WHEELER, JR. and R. A. SANDSTEDT, *J. Amer. Chem. Soc.* **77**, 2025 (1955).
[2] C. M. WHEELER, JR., R. D. BEAULIEU and H. W. BURNS, *J. Amer. Chem. Soc.* **76**, 6323 (1954).

We have found that X-ray powder photographs of tetramethylammonium tetrafluoroborate and the alleged tetramethylammonium hydroxytrifluoroborates are identical and moreover have *d* spacings the same as those reported by previous workers for Me_4NBF_3OH (Table 1). This is not definite proof of identity since the OH^- ion being of similar size to the F^- ion, two compounds, ABF_4 and ABF_3OH, should have almost identical powder patterns assuming there is no distortion due to hydrogen bonding. As further proof, however, the infra-red spectra of all of the samples show no

TABLE 1.—*d* SPACINGS FOR TETRAMETHYLAMMONIUM FLUOROBORATES

Me_4NBF_4	"Me_4NBF_3OH"—1	"Me_4NBF_3OH"—2	Values obtained by WHEELER *et al.*[3]
6·31 (5)	5·89 (1)	6·28 (2)	5·82 (6)
4·85 (6)	4·835 (2)	4·78 (2)	4·83 (10)
4·09 (10)	4·07 (10)	4·12 (10)	4·08 (100)
3·12 (7)	3·145 (3)	3·13 (4)	3·13 (20)
—	—	—	2·90 (1)
2·78 (5)	2·750 (2)	2·77 (3)	2·76 (10)
—	—	—	2·61 (1)
2·497 (8)	2·497 (4)	2·493 (4)	2·48 (40)
2·295 (5)	2·310 (3)	2·305 (4)	2·29 (20)
2·136 (4)	2.120 (1)	—	2·21 (6)
1·943 (3)	1·947 (3)	—	1·93 (20)
1·885 (1)	—	—	1·85 (1)
1·650 (3)	1·654 (2)	—	1·64 (18)
1·557 (1)	—	—	1·55 (3)
1·369 (2)	—	—	1·36 (1)
1·339 (1)	—	—	—
1·301 (1)	—	—	—

Figures in parentheses are estimated intensities based on the strongest line = 10 except for last column where strongest line was put = 100.

hydroxyl bands. A sample of potassium hydroxytrifluoroborate clearly showed these bands at 3120, 2860, and 1630 cm^{-1}. The principal band in this compound is split, probably because of hydrogen bonding.

Potassium hydroxytrifluoroborate was prepared from potassium bifluoride and boric acid.[2] The alleged tetramethylammonium hydroxyfluoroborates were prepared as previously described[3] from hydroxytrifluoroboric acid (Sample 1) and from methoxytrifluoroboric acid (Sample 2). (Found for 1: C, 30·8; H, 7·90%. Found for 2: C, 30·2; H, 7·77%. Calc. for Me_4NBF_3OH: C, 30·2; H, 8·34%. Calc. for Me_4NBF_4: C, 30·4; H, 7·51%.) Tetramethylammonium tetrafluoroborate was prepared from 40% tetrafluoroboric acid and tetramethylammonium chloride (Found: C, 30·5; H, 7·83%).

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Inorganic Chemistry Research Laboratories
Imperial College London S.W.7

K. C. MOSS
D. W. A. SHARP

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On barium manganate and some related compounds

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IN recent years the structures of a few manganates(V) and ferrates(IV) have been studied, but no quantitative structural data appear to be known for manganates(VI) and ferrates(VI). GRIMM *et al.*[1]

[1] H. G. GRIMM, C. PETERS and H. WOLFF, *Z. Anorg. Chem.* **236**, 57 (1938).

found that barium manganate(VI) and ferrate(VI) are isotypic with barite; the lattice dimensions of $BaMnO_4$ and $BaFeO_4$ were stated to be almost identical, and larger than those of $BaSO_4$. KREBS[1] stated that the cell dimensions of $BaFeO_4$ and $BaCrO_4$ were equal within 1 per cent. However, we were unable to trace any quantitative data in the literature on the lattice constants of either $BaCrO_4$, $BaMnO_4$, or $BaFeO_4$, nor of $BaSeO_4$ which also possesses a barite-type structure.[2]

We have obtained this data (Table 1). The cell dimensions were determined by means of X-ray powder photographs taken with Cu Kα radiation in a camera of 114·6 mm dia.; the films were covered with an Al foil. All data refer to samples dried at 120°C; the accuracy is 0·010 Å.

TABLE 1.—LATTICE CONSTANTS OF $BaSO_4$, $BaCrO_4$, $BaMnO_4$, $BaFeO_4$ AND $BaSeO_4$

	a (Å)	b (Å)	c (Å)	V (Å^3)
$BaSO_4$	8·882	5·456	7·155	346·7
$BaCrO_4$	9·103	5·526	7·337	369·1
$BaMnO_4$	9·065	5·472	7·304	362·4
$BaFeO_4$	9·103	5·446	7·301	362·0
$BaSeO_4$	9·034	5·645	7·364	375·5

Barium manganate(VI) was prepared by a modification of the method described by SCHLESINGER and SIEMS.[4] After the slow addition of a saturated $KMnO_4$ solution to an equivalent proportion of a boiling saturated solution of $Ba(OH)_2$, a large excess of $Ba(OH)_2$ solution was added, until the precipitate had completely turned green and the supernatant liquid colourless. The precipitate was washed by repeated decantation with dilute NaOH and then with water, and dried at 120°C; precautions were taken to exclude CO_2.

In attempts to prepare $BaMnO_4$ by SCHLESINGER and SIEMS'[4] original method, we invariably obtained violet to black products, which are not pure $BaMnO_4$, but mixed manganates(VI,VII) with some admixed MnO_2. The unit-cell constants of these mixed manganates(VI,VII) are significantly larger (approximately 0·5 per cent) than those of pure $BaMnO_4$. Coprecipitation of $BaCO_3$ could not entirely be avoided; this contamination, however, did not interfere with the unit-cell determination and $BaCO_3$ could even be used as an internal standard.

Originally we surmised the mixed manganates(VI,VII) to be solid solutions, $(Ba,K)MnO_4$, in analogy to $(Ba,KH)SO_4$.[5] However, spectroscopic analysis showed that less than 0·05 at.% of Ba was substituted by K, which is far too little to account for the observed dilation of the lattice. (Compare $KMnO_4$, barite-type; $a = 9{\cdot}098$, $b = 5{\cdot}730$, $c = 7{\cdot}394$ Å.[6]) No other contamination was found. However, the mixed manganates(VI,VII) retain some water, even more persistently than do $BaFeO_4$,[7] $BaCrO_4$, and $BaSO_4$.[8] Therefore, they probably may be formulated as

$$(Ba_{1-x},H_2O_x)\{(Mn^{VI}_{1-2x},Mn^{VII}_{2x})O_4\}.$$

The Ba^{2+} ion and H_2O are of approximately the same size and several phases are known in which Ba^{2+} can be partly substituted by H_2O. It may be noted that solid solutions $BaSO_4$—$Ba(MnO_4)_2$ have been prepared,[1] which may be analogues of the mixed barium manganates(VI,VII).

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We also tried to prepare $BaMnO_4$ by the method described by AGLADZE and BERIKASHVILI.[9] Intimate mixtures of $Ba(NO_3)_2$, MnO_2, and a trace of Na_2CO_3 were heated at 600°C for several hours. The emerald green reaction products consisted mainly of barium manganate(V). $Ba_3(MnO_4)_2$ is isotypic with $Ba_3(PO_4)_2$;[10] the dimensions of the rhombohedral unit cell were found to be: $a = 5{\cdot}695$, $c = 21{\cdot}48$ Å, in agreement with KLEMM.[11]

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F. JELLINEK

Laboratorium voor anorganische chemie
Rijksuniversiteit Groningen
The Netherlands

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Chemical state of radiochlorine formed by the $^{41}K(n,\alpha)^{38}Cl$ reaction

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ONE of the important observations made in the course of the study of the Szilard–Chalmers process in solids is the difference between the fate of the radio-halogen in chlorate and iodate crystals after irradiation with thermal neutrons. In solid chlorates the retention is very low[1] and in iodates—with the exception of ammonium iodate—it amounts to about 67%.[2] It was a point of interest to see whether this difference should be attributed mainly to the chemical properties of the radio-halogen or to those of the crystal lattice. This question suggested to us a study of the irradiation of potassium iodate with fast neutrons to form ^{38}Cl in a surrounding of iodate ions.

The result of the experiment indicated that practically all of the ^{38}Cl was present as chloride ions (or possible chlorine atoms), at any rate less than 1% of the chlorine activity was found in the chlorate fraction. Thus radiochlorine in an iodate lattice behaves in a manner very similar to that of radiochlorine in a chlorate lattice.

Experimental

Potassium iodate was irradiated with D + Be neutrons in the cyclotron of this institute. The crystals were dissolved in water containing chloride and chlorate. This solution was extracted several times with carbontetrachloride containing iodine and this treatment was followed by repeated precipitations of barium iodate. (The last precipitate was found to be practically inactive.) At this stage nitric acid was added and one or two precipitates of silver chloride obtained. Then the chlorate was reduced by boiling with sulphite and a silver chloride sample precipitated which contained the chlorate-^{38}Cl. All samples were counted with a Geiger–Müller counter and decay curves were obtained in all cases. All samples had identical weights and sizes which eliminated corrections for self-absorption.

The activity in the chlorate AgCl was quite low, but not negligible. It was evident, however, from the observation of the long period of ^{130}I that this activity was mainly due to the presence of some radioactive iodine. (Three hours after the irradiation the total iodine activity — $^{130}I + ^{126}I$ — is about 20 times as strong as the chlorine activity.) As the activity of the last iodate precipitate was quite low, this radioiodine probably came from a different iodine compound which is not recognized in our analysis. As the decay curve of the radioiodine was known with fair accuracy (the ratio of ^{130}I to ^{126}I differs somewhat in various fractions) we were able to apply a correction for the presence of radioiodine in the chlorate fraction, which showed that the ^{38}Cl activity in this fraction was negligible compared to that in the chloride.

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Institute for Nuclear Physics Research
Amsterdam
The Netherlands

M. VLATKOVIĆ
A. H. W. ATEN, JR.

Extraction of the lanthanides as their di-n-butyl orthophosphates

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SEVERAL recent publications are concerned with the extractive properties of mono- and di-alkyl orthophosphoric acids.[1–6] The investigations have revealed the selectivity of these reagents in the extraction of metallic cations and interesting facts about the structures of the complexes formed.

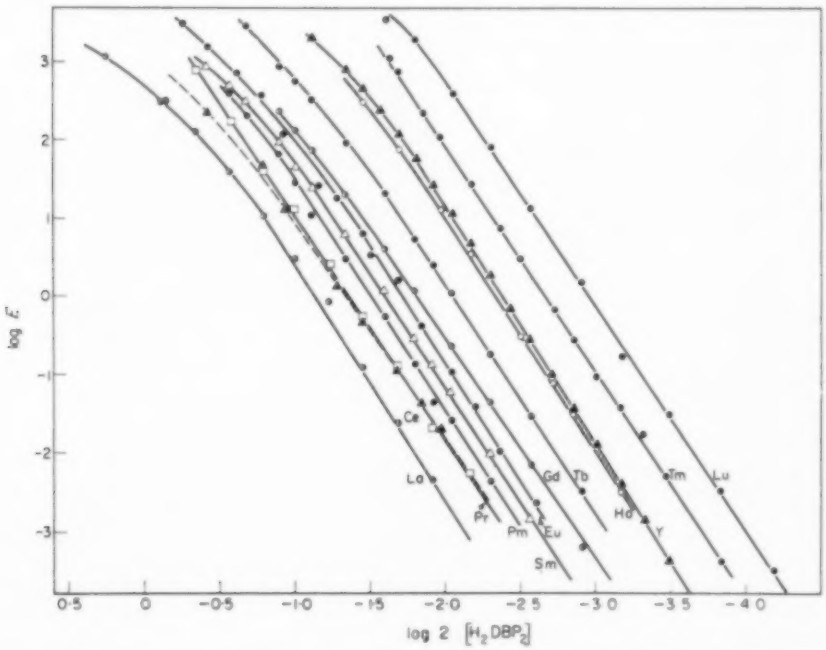

FIG. 1.—Variation of log E with log $2[(HDBP)_2]$ at $HClO_4$, 0·1 N. Solvent: butylether.

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We have investigated during the last three years the extraction of the lanthanides into solutions of di-n-butyl orthophosphoric acid (HDBP) in a carrier solvent such as dibutylether from aqueous $HClO_4$. The distribution ratio E of a cation between the two phases was determined radiometrically. Experiments were performed with tracer quantites of ^{140}La, ^{144}Ce, ^{142}Pr, ^{147}Pm, ^{153}Sm, $^{152,154}Eu$, ^{153}Gd, ^{160}Tb, ^{166}Ho, ^{170}Tm, ^{177}Lu and ^{91}Y.

In order to be able to derive the formula of the complex which is formed, from a curve of distribution ratio versus reagent concentration at a fixed pH, it is necessary to determine as a function of the concentration the distribution of the reagent between the two phases at this fixed pH.[7]

The distribution of HDBP between an aqueous phase 0·1 N in $HClO_4$ and dibutyl ether has been measured at initial concentrations in the organic phase ranging from 10^{-6} to 0·6 M/l; in agreement with conclusions published by Dyrssen for chloroform and hexone, the distribution curve can be interpreted on the basis of dimerization of HDBP in the organic phase. In dibutylether the observed dimerization constant is $1{\cdot}5 \times 10^9$ $(M/l)^{-1}$ and the distribution coefficient of the monomer between the two phases is 0·7. For carbon tetrachloride, these two constants are 7×10^4 $(M/l)^{-1}$ and 0·2. These experiments were performed with HDBP labelled with ^{32}P.

Fig. 1 summarizes our results for the distribution ratio as a function of the concentration of dimeric $(HDBP)_2$ in equilibrium in the organic phase for several rare earths and for yttrium. Except for Ce^{3+}, the curves are parallel and linear over most of the range, with a slope of 3; this indicates that the complex forming reaction is as follows in agreement with conclusions reached by other investigators.[3-6]

$$Me^{3+} + 3(HDBP)_2 \rightleftarrows Me[H(DBP)_2]_3 + 3H^+$$

The separation factor r (ratio of the distribution E for two adjacent lanthanides) is found to be 2·6 for the heavy rare earths and 1·95 for the light elements. PEPPARD[3] has found 2·5 for the whole series in the case of extraction by a solution of di-2-ethylhexyl phosphoric acid in toluene.

In spite of all precautions taken to keep the ion in the trivalent state, the curve for Ce in Fig. 1 shows a different slope; this point is being investigated more thoroughly. Work is also in progress on the transuranium elements.

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G. DUYCKAERTS
PH. DRÈZE*
A. SIMON*

Laboratory of Analytical Chemistry
University of Liége

* Chercheurs agréés à l'Institut Interuniversitaire des Sciences Nucléaires. Belgium.

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LETTER TO THE EDITOR

Slow isotopic exchange of chelate compounds of indium in water and in anhydrous organic solvent

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As an extension of our work on the isotopic exchange of metal ions in co-ordination compounds,[1] we have examined the exchange of indium, by the use of ^{114m}In (half-life, 49 days) as tracer, since the isotopic exchange reactions of the gallium group elements have not been studied.[2] The exchange in water was examined between the indium ion and its chelate with N-2-hydroxyethyl-ethylenediamine-NN′N′-triacetic acid (EDTA-OH) labelled with ^{114m}In at various pH values.[3] The indium ion is separated from its EDTA-OH complex by precipitating indium oxinate at pH 4. The indium oxinate is weighed on a sintered glass filter plate and submitted to γ-ray scintillation spectrometry for the specific counting rate to be measured by the use of the photo-electric peak due to 0·192 MeV γ-rays.

The results of the kinetic study are summarized in Table 1, in which the exchange rate is expressed by

$$R = -2{\cdot}303/t \,.\, ab/(a+b) \,.\, \log_{10}(1-F)$$

according to McKay.[4] Here a and b stand for the molar concentration of the indium ion and the EDTA-OH complex respectively, and t and F for the lapse of time and the fraction of exchange, respectively.

TABLE 1.—RATE OF ISOTOPIC EXCHANGE OF INDIUM BETWEEN THE INDIUM ION AND ITS EDTA-OH COMPLEX IN WATER

pH	Concn. of H^+	Half-life	R mole/hr	$R/[H^+](\times 10)$
1·85*	$1{\cdot}4 \times 10^{-2}$	10 min	$1{\cdot}8 \times 10^{-3}$	1·3
2·62	$2{\cdot}4 \times 10^{-3}$	138 min	$1{\cdot}4 \times 10^{-4}$	0·6
2·85*	$1{\cdot}4 \times 10^{-3}$	176 min	$1{\cdot}0 \times 10^{-4}$	0·6
3·44	$3{\cdot}6 \times 10^{-4}$	6 hr	$6{\cdot}1 \times 10^{-5}$	0·7
4·64	$2{\cdot}3 \times 10^{-5}$	48 hr	$5{\cdot}9 \times 10^{-6}$	2·6
5·80	$1{\cdot}6 \times 10^{-6}$	7 days	$1{\cdot}8 \times 10^{-6}$	11
8·05†	$8{\cdot}9 \times 10^{-9}$	>20 days	$<10^{-6}$	$>10^3$

Conditions: $\mu = 0{\cdot}1$ (KNO_3); $[In^{3+}]$, $0{\cdot}7 \times 10^{-3}$; [In·EDTA–OH·H_2O], $0{\cdot}9 \times 10^{-3}$.

* Acetate buffer, 0·03 M, others tartrate buffer, 0·005 M.

† Becomes turbid after 3 hr; temperature 25 ± 1°C.

It is obviously seen that at room temperature the isotopic exchange proceeds with a measurably slow rate, which depends on the hydrogen ion concentration. In an acid solution of pH less than 4, the rate appears to be proportional to the hydrogen ion concentration, but not at a pH more than 4.

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This finding might be correlated with the facts that the formation of a metal chelate compound is favoured in a solution of higher pH value and that the indium EDTA-OH complex has one mole of co-ordinated water, which has an apparent dissociation constant of 2×10^{-6} and begins to produce a hydroxy complex at about pH 5. A similarly slow isotopic exchange appears to take place between the indium ion and its ethylenediaminetetraacetate complex.[5]

TABLE 2.—RATE OF ISOTOPIC EXCHANGE OF INDIUM BETWEEN OXINATE AND ACETYLACETONATE IN CHLOROFORM

Concn. of oxinate	Concn. of acetylacetonate	Half-life (min)	*R*(mole/hr)
$3{\cdot}07 \times 10^{-3}$ M	$2{\cdot}51 \times 10^{-3}$ M	11	$5{\cdot}5 \times 10^{-3}$

Temperature, 25°C.

The isotopic exchange was also studied between indium oxinate (labelled with ^{114m}In) and acetylacetonate in anhydrous chloroform. The former is precipitated free from the latter on addition of petroleum hydrocarbon. It is similarly weighed and the specific counting rate measured. Since indium acetylacetonate readily undergoes hydrolysis, care was taken to keep the compounds and the solvents completely anhydrous and the whole procedure was carried out in a dry box (relative humidity, less than 15 per cent). The result is shown in Table 2; the exchange proceeds with a measurably slow rate at this concentration.

Because the solubility of the chelates in chloroform and the concentration range in which precipitation of pure oxinate is effected are limited, further kinetic study may involve some experimental difficulty.

Institute for Nuclear Study
The University of Tokyo
Tanashi, Tokyo

K. SAITO
M. TAMURA

[5] K. SAITO and the late H. TERREY, *J. Chem. Soc.* 4701 (1956).

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